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THE CHEMISTRY AND TECHNOLOGY OF HIGH EXPLOSIVES

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**PART 1
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systematization
This book provides a ~~XXXXXXXXXX~~ of data on the properties and
methods of production of high explosives. The theoretical principles of the
production processes are examined, and the states of the high-explosives industry
abroad is described on the basis of literature data.

The book may be ~~XXXXXXXXXX~~ recommended for students in the chemical
engineering institutions of higher education, as a text. It may also be
employed as a practical and reference manual for engineering, technical, and
~~XXXXXXXXXX~~ scientific personnel in the explosives industry.

Reviewers. Professors I.Ye.Moysak and S.L.Simonenka, Candidate in Engineering Sciences

Editor, Docent G.A.Avakyan, Candidate in Engineering Sciences

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About twenty years have elapsed since the appearance of the noted monograph, "The Chemistry and Technology of Nitro Compounds" by A.G.Gorst. In the intervening years, the chemistry and technology of explosives has undergone considerable development, and the production of explosives has become an important branch of the chemical industry.

The growth in the production of explosives would be inconceivable without a correspondingly rapid progress in the chemistry and technology of, and in the first instance, without the developments of the theoretical principles governing the processes of nitrating.

In recent years, the foreign press has conducted a broad discussion of problems of the chemistry and, in some part, of the technology of explosives. A major contribution has been made by the works of Soviet chemists, and in particular those of Academician A.V.Topchiyev and A.I.Titov. Specifically, the theory of nitrating developed by A.I.Titov, based upon the most recent studies of the nature of nitrating mixtures makes it possible to elaborate rational technological processes for the production of explosives.

The Soviet literature lacks works generalizing the theoretical and experimental data on the chemistry and technology of explosives accumulated during the past twenty years. The author hopes that this book ~~will~~ will, in part, fill this ~~lacuna~~ lacuna.

The book before you systematizes the ~~data~~ data on the properties and methods of

production of high explosives, examines the theoretical ~~XXX~~ foundations on which
based,
the technological processes are ~~XXXXXXXX~~ and reflects the state of the production
of high explosives abroad, as revealed in the literature.

The book consists of three parts, embracing the three most important classes
of explosives. The first part describes nitro compounds, the second nitroamines,
and the third nitric esters.

In the first chapter of each part, the general properties of the explosives
of the given class are illuminated, as are the theoretical fundamentals of the
process by which they are produced. Further, a description of the ~~XXXXXXXX~~ chemistry
and technology of the most important representatives of this class is then
presented.

In the first part, in addition to the foregoing, ~~there is~~ a description
of the kinetics of the process of nitration in ~~XXXXXXXX~~ homogeneous
and heterogeneous
conditions is provided, as well as the nitration process flow and the acid
equipment of the high-explosives plant.

The author wishes to express his profound gratitude to his teacher,
A.G.Gorst, whose book, "The Chemistry and Technology of ~~XXXXXXXXXXXX~~ Nitro Compounds"
as the example on which this monograph was constructed. The author is also
deeply indebted to K.K.Andreyev, A.S.Bakayev, G.I.Mel'nikov, N.Ye.Moysak,
V.N.Nazarov, S.L.Simonenko, and A.I.Titov, for their criticism and advice.

The author wishes to express his particular ~~XXXXXXXX~~ acknowledgement ~~XXXX~~
to the Scientific Editor of this ~~XXXX~~ book, G.A.Avakyan, who, in addition to a
most careful examination of the work and the ~~XXXXXXXX~~ introduction of the

necessary corrections and additions, is also responsible for the compilation of the tables of explosives and thermochemical values for explosives, and for the raw materials and intermediates thereof.

The author will be grateful for any and all critical remarks and suggestions.

INTRODUCTION

The term ^{high} ~~explosives~~ ^(HE) is applied to systems which tend, under external influence, to undergo exceeding rapid chemical transformation accompanied by the liberation of much heat and of gases to high temperatures, which gases are capable of performing work of displacement ^{or} ~~and~~ destruction. Unlike the combustion of the common fuels, the explosion reaction in ^{high} explosives occurs without participation of atmospheric oxygen.

High Explosives are concentrated energy sources and are therefore employed in various branches of the economy. The oldest branch of application is mining. Today, explosives are also employed in construction, the peat, petroleum, and other ~~branches~~ branches of industry, as well as in agriculture. Explosives are ~~very~~ extensively employed in warfare and therefore, that branch of industry underwent exceptional development during the Second World War.

The technology of explosives has, as its field of investigation, the methods and processes involved in the production of these circumstances. The technological flow of explosives production processes is based upon the properties of the starting, intermediate, and final products, and is determined by the nature of ~~the reactions taking place~~ ^{reactions taking place} ~~the reactions occurring~~ (the heat effect, liberation of gases, etc.).

Various factors are involved in determining the technological process flow in explosives production, and development of the least dangerous and most economical process is possible only with due consideration ^{these} to/factors.

In developing the technology, selecting the raw materials, the apparatus, equipment, and tools, all dangerous operations must be treated separately,

and the necessary safety measures must be ~~be~~ provided for in carrying them out.

Automatic monitoring and control, electronic equipment and automatic lock separation must be made extensive use of in the dangerous operations. This will also facilitate adherence to the flow sheet. Complete automation, including automatic monitoring and automatic control, facilitates the carrying out of the desired objectives, and safety in the work.

Origin
1. ~~MANUFACTURE~~ and Progress of the Manufacture of ^{High} Explosives

The explosives industry came into being in the second half of the Nineteenth Century, but its significant developments occurred only in the ~~XXXX~~ Twentieth Century, on the basis of the ~~XXXX~~ extraordinary growth of the basic chemicals industry, as well as of the coke chemicals and petroleum refining industries, which are the sources of the organic materials employed in the ~~XX~~ major high explosives.

It was the alcohol nitrates - ~~pyroxylin~~ and nitroglycerin, that were the first to appear. At the end of the Nineteenth and the beginning of the Twentieth Century, nitro derivatives of ~~XXXXXXXXXX~~ aromatic compounds (picric acid, trinitrotoluene, tetryl, ~~XXXXXXXXXX~~ etc.), whose properties render ~~XX~~ them considerably less dangerous in production and handling, were incorporated into the arsenal of arms. The fact ~~that~~ ^{more} that they could be handled/safely made it possible to employ them widely in filling shells.

In the period during which World War I was in preparation, the countries that were to launch it ^{stock piled} prepared large quantities of munitions. However, the consumption of shells was greater than had been presumed. It became clear that artillery fire was the most ~~XXXX~~ destructive of means and inflicted the greatest

losses.

The expenditure of munitions in the period 1870 - 1918 is illustrated in

Table 1.

Table 1

Period	Country	Quantity of Shells, Million Tons
1870-1871 (Franco-Prussian War)	Prussia	0.68
1904-1905 (Russo-Japanese War)	Russia	0.98
1914-1918 (World War I)	Russia	50
The same	Austro-Hungary	70
"	England	170
"	France	190

The high consumption of munitions during the First World War induced an increase in the explosives industry. Many polynitro compounds of the aromatic hydrocarbons obtained in the coking of coal and the pyrolysis of petroleum, were made use of in munitions. In order to satisfy the rising demand for explosives, mixtures based chiefly on ammonium nitrate came into wide use for the filling of shells.

The Second World War required an even greater quantity of explosives. The consumption thereof greatly exceeded that during the First World War. Thus for example, in 1910, the world production of explosives constituted 390,000 tons; whereas a considerably larger volume than this was produced in Germany alone during World War II, as is evident from Table 2

Table 2

a)	b)	
	c)	d)
1942	283.0	150
1943	410.0	238
1944	466.6	256

a) Germany, years; b) Production in thousands of tons; c) Explosives (including NH_4NO_3); d) Powder

However, production of explosives even on this scale in Germany did not satisfy the needs of the ~~fronts~~ fronts, which came to 600,000 tons a year. As is evident from the data presented, this figure was not reached. The effort was made to meet it by a wide use of ersatz materials. The shortage of explosives, (about 10,000 tons per month) was substituted for by the use of table salt (a mixture of 50% TNT, 46% table salt, and 4% of a special emulsifier was employed to fill artillery shells).

The acute shortage of explosives resulted in efforts to extend the list thereof by employing new types of raw material, but these efforts did not meet with success. We note only nitroguanidine, production of which came to 2000 tons a month in 1944. However, nitroguanidine did not gain extensive popularity as an explosive, but was employed chiefly in the powder industry.

Thus, despite the substantial expansion of the scale of production, German industry did not cope with the problem of providing the army with quality explosives in sufficient quantity.

In the United States, ^{331,000,000} ~~331,000,000~~ shells, ^{377,000,000} ~~377,000,000~~ mines, 5,900,000 tons of aviation bombs, and tens of millions of tons of other munitions, were manufactured in the course of World War II.

TNT was the major high explosive employed during the Second World War. Whereas, during the First World War, other ~~nitro~~ nitro derivatives of the aromatic hydrocarbons were employed along with TNT, in considerable quantities, during the Second World War, TNT or explosive mixtures employing it as base (ammonites, alloys of TNT and hexogen, etc.) were used particularly extensively. Thus, the share of TNT in the German industry

was more than 50% of the output of all explosives, as is clearly evident from

Table 3 (Bibl.1).

Table 3

a)	b)	c)
d)	18 600	21 000
e)	2 470	7 000
f)	280	400
g)	820	1 460
h)	18	30
i)	450	850
j)	1 580	5 000
k)	22 216	35 780

^{High}
a) Explosive; b) Production, June 1943, tons; c) Production planned for June 1944, (RDX) tons; d) TNT; e) Hexogen; f) Picric acid; g) PETN; h) Tetryl; i) Hexanitrodiphenylamine; j) Dinitrobenzene; k) Total

These data show that the most powerful explosives - hexogen and PETN, which were not employed in World War I, were widely used in World War II. Particular attention was given to developing the industry producing substances in countries that did not have sufficient resources for the production of explosives based on aromatic compounds. For example, in Italy, mass production of hexogen and PETN began as early as 1932 - 1933. Both these substances were employed by the Italians for the filling of munitions, not only in the pure or phlegmatized form, but in mixtures with ammonium nitrate. In Germany, hexogen was widely employed to fill ~~armor-piercing~~ armor-piercing and shaped-charge shells. PETN and RDX were also produced in France, ~~Czechoslovakia~~ Czechoslovakia, ~~USA~~ Canada, and the USA.

Like the First World War, the Second again required extensive employment of ersatz filling of artillery munitions, and this in turn meant that detonating devices

- caps and detonators - had to be rendered more powerful. The most powerful explosives - PETN and RDX - came to be employed therein.

2. Classification of High Explosives

Today, a large number of high explosives are known, but only a few of them are of practical significance.

Explosives may be solid, liquid, or gaseous. Examples of solid explosives are TNT, picric acid, and pyroxylin. Liquid explosives include nitroglycerin, nitroglycol, and a solution of nitrobenzene in nitric acid. Gaseous explosives include a mixture of hydrogen and oxygen, methane and air. ~~Only~~ Only solid and liquid explosives have achieved practical employment in engineering and military affairs.

8 In their applications, explosives may be classified into four groups:

- 1) initiating explosives; ^(initiators) 2) high explosives; 3) propellant explosives or powders;
- 4) pyrotechnical mixtures. The present volume shall examine only high explosives.

In composition, high explosives are classified into two large groups: chemical compounds and explosive mixtures. [#] The first group includes the following important classes of explosives:

a) Nitro compounds, which are organic compounds containing one or several C-NO₂ groups. The polynitro derivatives of aromatic compounds are of the greatest significance. A considerable portion of the nitro compounds of the aliphatic hydrocarbons are also explosives, but only a few are of practical significance;

b) Nitroamines, which are organic compounds containing the group N-NO₂;

c) Nitric esters, which are organic compounds containing the O-NO₂ group.

The nitric esters of alcohols and carbohydrates are employed as explosives;

d) Nitric acid salts. The most widely employed is ammonium nitrate (NH₄NO₃), as well as the nitrates of organic compounds [4] (guanidine, urea, methylamine etc.).

The second group is comprised of explosive mixtures containing or not containing explosives.

The most important classes of explosive mixtures containing explosive components include:

Ammonites.

a) ~~XXXXXXXX~~ or ammonium nitrate explosives, consisting of mixtures of ammonium nitrate and nitro compounds;

b) Alloys and mixtures of nitro compounds;

c) Nitroglycerin explosives (dynamites);

d) Chlorate and perchlorate explosives - mixtures of salts of chloric or with chlorous acids/nitro compounds, etc.

The mixtures consisting of nonexplosive components include combustibles and substances containing substantial amounts of oxygen or some other oxidizer.

Under these circumstances, the explosion reaction consists of oxidation of the elements composing the combustibles by the oxygen in the oxidizers. Explosive

mixtures of non-explosive components may be ~~XXXXXXXX~~ classified as follows:

a) smoking powders - mixtures of ~~XXXXXXXX~~ ^{saltpeter} and coal; b) oxyliquids, mixtures of liquid air and combustibles; c) Mixtures of concentrated nitric acid or some other liquid oxidizer with combustibles.

nitrate

The ammonium ~~XXXXXXXX~~ explosives are the most important in the category of

explosive mixtures.

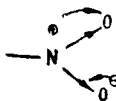
Artillery poses very rigid specifications for high explosives. They must be highly powerful, safe to handle, be sufficiently sensitive to the initial impulse, and stable in storage. In addition to all the foregoing, high explosives used in armaments must have an adequate ~~XXXXXX~~ availability of raw materials, and the method of production must be sufficiently simple and safe.

The explosives currently employed are far from ~~XXXXXXXX~~ satisfactorily meeting the requirements indicated and, therefore, the search for new powerful explosives having the properties indicated above is a very important problem for the scientists and engineers working in this field. Equally urgent is the problem of improving the technology of explosives production to reduce the danger involved in manufacture and to increase labor productivity and, as a consequence, to reduce the cost of the product.

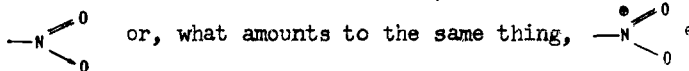
PART I

I. NITRO COMPOUNDS

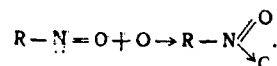
Nitro compounds are substances containing the nitro group (NO_2). In these compounds, nitrogen is attached directly to the carbon atom of the molecule. Both oxygen atoms and nitro group are of equal ~~IX~~ importance, and therefore the structural formula appears as follows:



However, the structure of the nitro group is now believed to be



This structure will become comprehensible, if it is assumed that the nitro group is formed from the nitroso group, as follows.



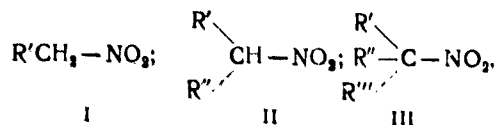
Herein, an electrostatic reaction arises between the nitrogen atom and the second oxygen atom, because, in establishing the valence bond, the nitrogen atom expended, not one electron from its outer shell, as occurs in the ordinary kind of ~~ordinary~~ covalent bond, but two, and thus acquired one positive elementary charge. However, the oxygen atom, not only did not yield a single electron for formation of the doublet attaching it to the nitrogen, but acquired

one electron of the free nitrogen pair, i.e., it acquired one elementary negative charge. Thus, the bond between the second atom of oxygen and the nitrogen is a semipolar bond.

Nitro compounds are isomeric ~~XXXXXXXX~~ with respect to the nitric esters R-ONO, containing the monovalent radical O-N-O, isomeric to the nitro group.

The nitro group usually strengthens the acid properties of organic compounds, tending to give them or to reinforce polarity. The presence of the nitro group complicates the nitration, sulfonation, chlorination, Friedel-Crafts, and similar reactions. In the aromatic nitro ~~XX~~ compounds, the nitro group directs substituents chiefly into the meta position.

In terms of the number of nitro groups, nitro ~~XXXX~~ compounds are classified as mono-, dinitro- compounds, etc. The mononitro compounds, ^{as} ~~are~~ the aliphatic series R-NO₂ are classified, depending upon the type of radical, into primary (I), secondary (II), and ternary (III) compounds:



The aromatic nitro compounds form various isomers which differ from each other in terms of the relative positions of the nitro and other groups in the benzene ring.

CHAPTER I

GENERAL DESCRIPTION OF THE AROMATIC NITRO COMPOUNDS

The polynitro compounds of the aromatic series, such as TNT, TNX, ~~XXXXXXXXXX~~ dinitrophenol, etc., are ~~XXXXXX~~ explosives and have found wide application in practical use. The ~~XXXX~~ C-NO₂ bond is of adequate stability, and it makes for the high stability of the nitro compounds (for example, TNT ~~XXXX~~ does not decompose at temperatures of up to 150°). The ~~XXXXXX~~ explosives in this class are of comparatively low sensitivity. All the aromatic ~~XXXXXXXXXX~~ polynitro compounds are solids, which makes it easy to use them in various types of munitions, particularly shells.

The starting material for explosives of this class consists of aromatic hydrocarbons, phenols, and nitrating mixtures. Aromatic hydrocarbons are produced in substantial quantity directly in the coke, chemical, and ~~XXXXXXXXXX~~ petroleum ~~XXXXXXXXXX~~ industries, and phenols are obtained synthetically, for the most part, from benzene, which is also a product of the coke chemical and petroleum industry. The ~~XXXXXX~~ synthesis of nitro compounds does not present major difficulties. The synthesis of nitro compounds of the phenols is somewhat more complex and requires special precautionary ~~XXXXXXXXXX~~ measures, due to certain specific properties ~~XXXXXXXXXX~~ thereof.

The aromatic nitro compounds are produced by nitrating the ~~XXXXXXXXXX~~ corresponding compounds by a mixture of sulfuric ~~XXXX~~ and nitric acid. Technically, the nitro product is rarely ^a pure substance. Usually, a mixture of various isomers results in the course of production.

^{Monos}
Nitro compounds are widely employed in the aniline dye industry as starting products ^{for} ~~where~~ production of corresponding amines. They are also manufactured in large ~~XX~~ quantities in the explosives industry, as they are, in addition, intermediates for the production of polynitro, compounds - the basic high explosives. In the past, mononitro compounds used to be added, as an independent product, to the explosive trinitro compounds. For example, ~~XX~~ mononitro naphthalene was employed in an alloy with picric acid, to phlegmatize the latter. The mononitro compounds do ~~XX~~ not have explosive properties.

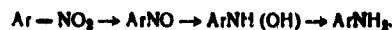
The dinitro compounds do have explosive properties. Some of them are employed in explosive mixtures. However, they are not employed independently as explosives. As indicated above, the dinitro compounds are explosives. The tetranitro compounds are also explosives, but are less stable and more sensitive to mechanical action, and therefore they do not, as a rule, have practical value.

11 Explosives of the nitro compound class have a number of common properties.

A characteristic reaction for them is the reduction reaction

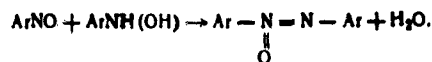


~~XXX~~ Reduction of the nitro compounds takes place through the medium of a number of intermediate stages. In an acid medium, ~~XX~~ reduction proceeds energetically, first to the stage of nitroso compounds and then to the stage of the derivative hydroxylamine, further reduction of which ~~XX~~ yields the amine:

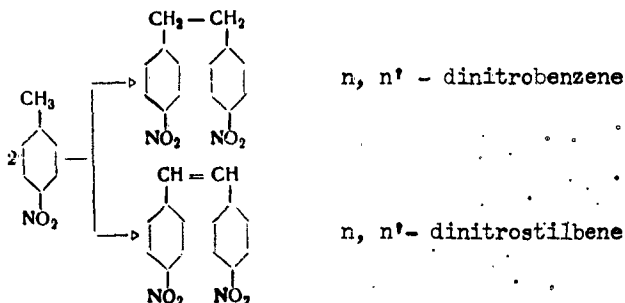


In an alkaline medium, reduction goes less energetically. Its terminal

products are the nitroso compound and the derivative hydroxylamine, which undergoes condensation into the nitroso compound:



In certain cases, the reduction reaction of nitro groups attached to an aromatic ring, proceeds in special fashion. If the nitroso compound undergoing reduction contains the methyl group in para position relative to the nitro group, one or two atoms of the hydrogen of the methyl group will cleave off, resulting in the formation of dibenzyl and stilbene derivatives (Bibl.2):



Nitro compounds do not react with dilute sulfuric acid. However, with the concentrated acid they form salt-like ion compounds, such as $[\text{C}_6\text{H}_5-\overset{\oplus}{\text{N}}(\text{OH})] \text{HSO}_4^-$. They react, in similar fashion, with aluminum chloride and like substances. Mononitro compounds react more readily with sulfuric acid than do the di- and trinitro compounds. The formation of complexes containing H_2SO_4 makes it difficult to nitrate them, whereas complexes with AlCl_3 create difficulties in alkylation and acylation in accordance with the Friedel-Crafts reaction.

Because they contain acid nitro groups, the polynitro compounds are capable of reacting with the caustics, the alkoxides, and ammonia, with formation

of tinted products of quinoid structure. This is the basis ~~for~~ for Yanovskiy's qualitative test for nitro compounds. He found that solutions of nitro compounds in alcohol or acetone with caustics yield a characteristic bright color (see Appendix 1 for the characteristic colors of nitro compounds in caustic solutions).

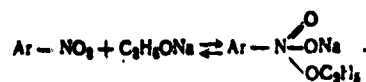
This reaction may be employed successfully to differentiate mononitro derivatives of benzene from the di- and trinitro derivatives. Thus, in the presence of acetone and alkali hydroxides, the mononitro compounds of this series do not color the solution, the dinitro compounds give it a reddish violet color, and the trinitro compounds cause it to become blood red. The color reaction ~~may~~ ^{may} be lacking if a large number of substituents are present, as is the case, for example, in trinitro~~methylene~~ ^{xylene}.

12 A study of the Yanovskiy's reaction resulted in the discovery of a number of regularities: 2,4-dinitro compounds color ~~and~~ alkali ~~and~~ hydroxide in acetone solution sky blue, if a methyl group is in the ~~ortho~~ ^{ortho-} or para-position. However, if some other group is in this position, the coloration will be red. Di- and trinitro compounds whose nitro groups are in other positions than these form colorless solutions, or yield a pale yellow tint.

The presence of hydroxyl or amino groups in the ring inhibits the reaction. Acylation of the hydroxyl group yields no results, but introduction of the ~~alkoxy~~ ^{alkoxy} group instead of the hydroxyl eliminates the effects of the latter.

According to Hantzsch and Kissel (Bibl.3), the reaction of aromatic nitro derivatives with alcoholates and alcohol solutions of the caustics results in the

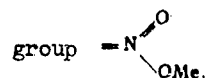
formation of salts of the following structure:



However, this structure ~~XXXX~~ does not explain the coloration of the resulting substances.

Meisenheimer (Bibl.4) suggested that under the effect of alcohol solutions of caustics, the benzoid form of the ring converts to the quinoid form, and the resultant ~~XXXXXXXX~~ ^{compound} is a salt of quinolonitric acid. Later, Hantzsch (Bibl.5)

pointed out that the sky blue coloration of the reaction products of aromatic nitro compounds and alcoholates is ~~XXXX~~ ^{due} to the presence of the following ~~XXXX~~



I.V.Stefanovich (Bibl.6) isolated mono-, bi-, and trimetallic derivatives of ~~XXX~~ 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 2,4,6-trinitro-*m*-xylene, ~~XXXXXX~~ 1,3,5-nitrobenzene, ~~XXXXXXXXXX~~ and 2,4,6-trinitrophenylmethylnitroamine and tetryl, and found that, except for tetryl, these substances attach themselves, in an ~~XXXXXX~~ anhydrous toluene-alcohol medium, to the molecule of the nitro compound in the molecule of the alcoholates of the alkali metals in a quantity equal to the number of nitro groups in the substance. It is proved possible only to attach three molecules of alcoholate to the tetryl.

When caustics act in the presence of oxidizers upon polynitro compounds containing a methyl group, the result is dark-brown substances of complex and ^{composition.} heterogeneous ~~XXXXXXXX~~ Copisarov (Bibl.7) regards them as derivatives of dibenzyl and stilbene resulting from nitro molecular oxidation and condensation.

In shock sensitivity, the metal derivatives of the aromatic nitro compounds approximate ^{that of} initiators, but their sensitivity to friction is considerably lower.

Some of them have very low flash points, for example, in the case of the ammonia derivative of TNT, it is approximately 50°.

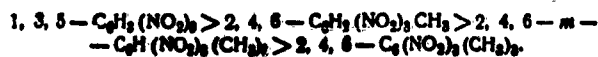
Korczynski (Bibl.8) showed that when ~~XXX~~ gaseous ammonia acts upon nitro derivatives of the aromatic hydrocarbons; the consequence, depending upon the conditions, will either be a salt or an addition product. At low temperature (of the order of -10°), salts are formed that contain more ammonia than might have been expected ~~XXXXXXXXXXXX~~ stoichiometrically.) Thus, for example, he obtained the following

salts: 2,6-C₆H₃(NO₂)₂OH · 2NH₃; 2,4,6-C₆H₂(NO₂)₃OH · 2NH₃; 2,4-C₆H₃(NO₂)₂COOH · 2NH₃; 1,3,5-C₆H₃(NO₂)₃ · 2NH₃ and various others. These salts are termed Korczynski's ~~XXXXXXXXXXXX~~ "abnormal" salts. In addition, addition products are obtained.

With increase in temperature, the "abnormal salts" dissociate into ammonia normal and ~~XXXX~~ "ammonia salts" which yield the initial nitro products under the influence of dilute mineral acids. The products of addition of ammonia to the nitro derivatives of the aromatic hydrocarbon also lose part of their ammonia when the temperature is raised, but neither in the presence of dilute mineral acids nor under other circumstances do they regenerate the original nitro derivative.

The presence of moisture, and of low temperature, significantly raise the ammonia reaction ~~XXX~~ rate.

The compounds studied may be arranged in the following series of diminishing sensitivity to ammonia:



Trinitrobenzene reacts almost instantaneously with anhydrous gaseous ammonia at 15°, but trinitroethylene does not change at all even when subjected for many hours to moist gaseous ammonia at 15°.

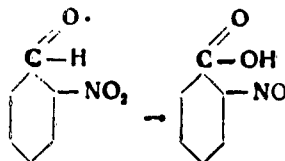
The accumulation of nitro groups in the nucleus facilitates reaction with caustic reactants, the new substituent being sent into the ortho- or para-position.

1,3,5-trinitrobenzene
Thus, (TNB) regularly yields picric acid upon oxidation in a caustic medium,

~~XXXXXXXX~~ 1,3-dinitrobenzene converts, with NH₂OH, into 1,3-dinitro-2,4-diaminobenzene.

13 Ortho- and para-dinitro compounds really exchange one of the nitro groups for a hydroxyl, alkoxyl, or amino group under the effects of caustics, alcoholates, or amines, respectively (Bibl.9).

Many aromatic nitro compounds, particularly those ~~XXXXXXXX~~ containing the nitro group in a side chain, are light-sensitive, and this results in shifting of the oxygen atom of the nitro group. Thus, light causes an ortho-nitrobenzoic aldehyde to undergo virtually complete conversion into ortho-nitrobenzoic acid:



Polynitro compounds undergo similar conversions due to light at the cost of the nitro groups/the ortho-position in the side chain. This usually is accompanied by ~~XXXX~~ the formation of ~~XXXX~~ dark-colored products (Bibl.10).

The effect of sunlight over a period of several months ~~is~~ upon a mixture of

~~XXXX~~

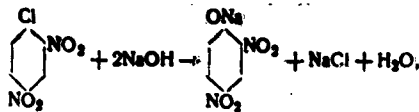
aromatic nitro compounds and other organic compounds will cause the nitro compounds to manifest their oxidizing ~~properties~~ properties. Thus, under the conditions described, a mixture of nitrobenzene and ~~naphthalene~~ naphthalene^{one} will reveal traces of ~~beta~~ β -naphthol, and a mixture of nitrobenzene and toluene to yield an insignificant quantity of ~~benzoic~~ benzoic acid and para-aminophenol. Nitrobenzene and aniline yield nitrosobenzene, phenylhydroxylamine, ~~ortho~~ para-aminophenol, ~~ortho~~ methoxybenzene, and ortho-methoxybenzene. When light is applied for a long period to a mixture of ortho-nitrotoluene and aniline, the consequence is the formation of para-aminophenol, 2-methoxybenzene, and ~~2-benzoate~~ 2-benzoate-metacresol. The light sensitivity of the nitro compounds has had rather detailed study (Bibl.11).

The nitro group improves the acid properties of a phenol ~~and~~ hydroxyl and reduces the basic character of the amino group, particularly in the ortho- and para-positions. Thus, for example, nitrophenols are stronger acids than are phenols. The basicity of the amino group in polynitro derivatives of aromatic amines drops so considerably that these compounds lose the capacity to form salts in combination with acids.

The ~~nitro~~ nitro group of aromatic compounds is capable of activating replacement groups and the hydrogen atoms of the benzene ring which are in the ortho- and para-positions relative thereto. The activating effect of the nitro group is expressed in weakening the bond of the second nitro group or another electrically negative substituent with the ring, and therefore these groups are readily replaceable by others.

For example, in ~~dinitrochlorobenzene~~ dinitrochlorobenzene^{one}, the chlorine is readily replaced by hydroxyl

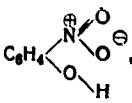
13 under the effect of 7% solution of caustic soda at a temperature of 100°C:



while the presence of a catalyst - copper - and a temperature of 300 - 375°C is required for the same reaction to occur in chlorobenzene, so that the process is to be conducted in an autoclave.

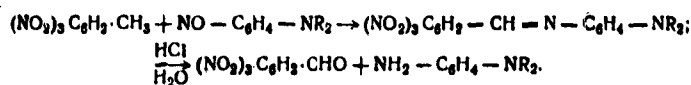
With increase in the number of nitro groups in the ring, their mobility usually increases, so that the possibility of replacing them improves.

In ortho-nitrophenols and ortho-nitroanilines, a hydrogen bond is formed of the

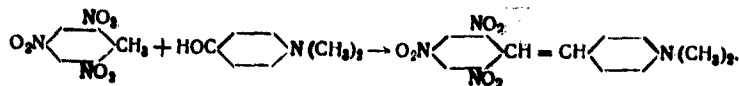
following type  with a consequence that bonds of this type differ from the para and meta isomers by lower boiling and fusion temperatures, greater volatility, more intense coloration, solubility in liquids of low polarity, etc. (Bibl.12).

14. Aromatic nitro compounds have a very pronounced capacity to form addition products. This capacity increases with increase in the number of nitro groups in the ring.

Methylized nitro derivatives go into condensation reactions with aromatic nitroso compounds and aldehydes. In the former instance, for example, upon condensation of TNT and 2,4,6-trinitrobenzaldehyde and dialkylphenylenediamine:



In the latter case, stilbene derivatives are formed in accordance with the following reaction



The polynitro^o compounds form complexes with the aromatic hydrocarbons, phenols, and esters thereof, with amines, etc. The complex compounds of polynitro compounds, particularly the picrates, are employed to identify aromatic compounds. The chemical structure of the substance and the nature of the substituents affect its explosive properties. The amount of internal energy increases with rise in the number of oxygen-containing groups (nitro-, oxy-, and others) and diminishes with the entry of groups not containing oxygen (CH₃, NH₂ and others). The shock sensitivity of aromatic nitro compounds rises with increase in the number of substituents in the ring. The influence of the CH₃ group is weaker than that of the OH, Cl, Br groups. The increase in shock sensitivity upon introduction of substituents testifies to the reduced stability of the benzene ring, facilitating the decomposition of the molecule.

All the aromatic nitro compounds have harmful effects upon the nervous system and dominantly upon the blood, and destroy the oxygen supply to the organism. Certain nitro compounds (for example dinitrochlorobenzene) also strongly affect the skin and give rise to skin affections (dermatites). The degree of harmful effects of the various nitro compounds varies. In the general case, toxicity diminishes with increase in the number of nitro groups, and, if that number is the same, with the presence of the methyl or the sulfo group in the ring, the toxic effect diminishes. For example, dinitrobenzene is more toxic than dinitrotoluene or dinitroxylene.

A characteristic sign of poisoning by aromatic nitro compounds is dizziness and headache. The poisoning takes place through the skin and the respiratory tract, due to the volatility of the nitro compounds. Quinine and oxygen are used in first aid in this type of poisoning (Bibl.13).

anhydride, nitric acid salt, or ^{introducing} to employ indirect methods of ~~forming~~ the nitro group [a review of indirect methods of nitration is presented in the work by Hodgson (Bibl.14)].

Section 1. Nitration with Nitric Acid

In general, the nitration reaction may be ~~xxx~~ represented as follows:



where ArH represents an aromatic hydrocarbon exchanging its hydrogen atoms for the NO₂ group. This equation presents an idea only of the results and not of the course of the reaction. The latter passes through a number of stages, and it is not the nitric acid itself, but its conversion products that enter into reaction with the aromatic compound.

Many compounds undergo nitration with extreme ease under the influence of nitric acid (phenanthrene, anthracene, naphthalene, phenol, etc.). However, the water liberated in nitration reduces the strength of the nitric acid and weakens its nitrating effect, as the nitration velocity constant depends upon the strength of the acid. Therefore, when nitric acid is used alone, as the nitrating agent, it proves impossible to make use of all of it. When the acid strength has been reduced to a specific level, the reaction virtually ceases. However, dilute nitric acid at elevated temperature (the temperature is increased to accelerate the nitration) frequently exercises more of an oxidizing than a nitrating effect upon an organic compound.

Reduction in temperature is a means of substantially reducing the oxidizing processes; as well as ~~the~~ ^{the} nitrating capacity of the nitric acid

15 diminishes to a lesser degree than its oxidizing action. This phenomenon is particularly noticeable when nitric acid acts upon readily oxidizable compounds, which are capable of being nitrated only at low temperature and in the presence of excess acid.

These circumstances sharply diminish the use of pure nitric acid in industrial practice.

16 Section 2. Nitration in the Presence of Water-Removing Substances

In order to avoid the harmful influence of dilution of the nitric acid, and to employ it more fully, water-removing substances are employed. That which is most generally employed in production is mixed sulfuric and nitric acid, in which the sulfuric acid serves to remove the water/^{and}simultaneously transforms the nitric acid into an active nitrating form. This permits a sharp reduction in the consumption of nitric acid per charge, reducing it almost to ~~XXX~~ that theoretically required for the formation of the nitro compound. Sulfuric acid has the further advantage that it reduces the oxidizing effect of nitric acid. The high boiling point of sulfuric acid makes possible, when necessary, the performance of nitration at high temperature. A technical advantage of mixed acid over nitric acid, of no mean importance, lies in the fact that it is capable of being stored in iron apparatus, as it does not induce corrosion, a factor of great importance in industrial practice.

Other than sulfuric acid acetic ~~XXX~~ anhydride, phosphorus pentoxide with polyphosphoric acid and boron trifluoride are employed as agents for ~~XXX~~ the removal of water (Bibl.15). As noted by Krater (Bibl.16), the cost of nitro products depends chiefly upon the method of removing water from the reaction zones and the method of recovering the water-removing substance. The cheapest product would be obtained if

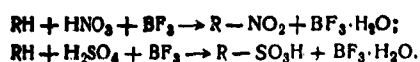
nitric acid alone were used for nitration, and if it were then neutralised, or if it were used in absorption towers ~~XXXXXXXXXX~~ for the production of nitric acid.

However, in view of the difficulties involved in the employment of this method, nitration is most frequently performed ~~XXXX~~ with a mixture of nitric/sulfuric acids, and with subsequent recovery of the latter from the spent acid.

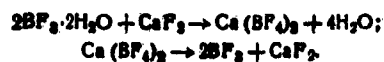
Other water absorbents, such as acetic anhydride, are very expensive due to the high cost of recovery and moreover, induce undesired side reactions complicating the purification of the end product. Acetic anhydride is used rather widely in the pharmaceutical industries, in the perfume industry, and also in the high explosives industry in the ~~XXXXX~~ manufacture of RDX as a water absorbent in nitration (Bibl.17).

In recent years, boron trifluoride, which is an active accelerator and dewatering agent in the processes of sulfonation and nitration has gained industrial use in the production of nitro compounds (Bibl.15).

When sufficient boron trifluoride is added, nitration and ~~XXXX~~ sulfonation may be performed by stoichiometric amounts of sulfuric ~~XXXX~~ and nitric acids. When this is done, the reaction proceeds as follows:



If, upon completion of the reaction, sufficient water is added to convert ~~XXX~~ $\text{BF}_3 \cdot \text{H}_2\text{O}$ into $\text{BF}_3 \cdot 2\text{H}_2\text{O}$, this latter compound may be driven off in vacuum as a heavy colorless liquid. ~~XXXX~~ Boron fluoride is liberated from the dihydrate by the addition of calcium fluoride and subsequent heating of the product by the reaction:



16 Section 3. Nitration by Nitric Acid Salts

In some cases, the nitric acid is replaced by salts thereof, which, when mixed with sulfuric ~~XX~~ acid, form nitric acid:



The advantage of this method lies in the fact that it makes possible the use of a completely anhydrous nitrating substance and, what is most important, one that does not contain nitrous acid. Nitrating mixtures of this type induce virtually no oxidation processes (Bibl.18, 19, 20), according to experiments conducted by 17 Prof. A.V.Stepanov and Academician A.V.Topchiyev. A shortcoming of these is the impossibility (at present) to make any use of the sodium bisulfate which is the nitration waste. From this point of view, it is more rational to employ ammonium nitrate, as the ammonium bisulfate can be used as ~~XXX~~ fertilizer.

More recent work (Bibl.21) refutes the conclusion that the intensity of the oxidizing processes is diminished upon nitration of toluene by a mixture of potassium nitrate and ~~strong~~ ^{conc.} sulfuric acid; the ^{resultant} ~~oxidational product yielded~~ was nitrotoluene and metanitrobenzaldehyde, the yield of which increased with increase in the temperature of nitration.

V.G.Georgiyevskiy (Bibl.22) found that the nitration velocity of aromatic compounds by a mixture of ~~XXXX~~ sulfuric acid and various salts of nitric acid depends upon the nature of the substance being nitrated, upon the nature of the nitrate salt, and upon the quantity of sulfuric acid. For example, when ammonium nitrate is employed, benzene undergoes nitration at a considerable velocity, whereas diphenyl virtually does not go into reaction at all. The effect of nitrate ~~salts~~ of strontium, barium, and copper

was
~~XX~~ studied. It was found that when benzene is nitrated to dinitrobenzene, the highest velocity is achieved when copper nitrate is employed. It has been proposed that nitration of organic silicon compounds be performed with copper nitrate (Bibl.23).

Nitrate~~s~~ salts are also nitrated in the presence of ammonium chloride and boron fluoride. The reaction rate in nitration with salts is always lower than in nitration with nitric acid (Bibl.18).

One of the methods of introducing the nitro group with the ~~XX~~ aid of salts of nitric acid is condensation of ammonium nitrate and formaldehyde, resulting in the formation of ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXX~~ cyclotrimethylenetrinitramine. The reaction is performed in an acetic anhydride medium and in the presence of boron fluoride as catalyst (Bibl.24).

It has been suggested that nitration be performed by stable nitronium salts such as nitronium tetrafluoroborate, hexafluorosilicate and hexafluoroantimonate (Bibl.25), as well as by nitryl chloride (Bibl.26).

Section 4. Nitration in the Presence of Acetic Acid

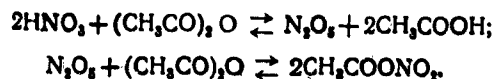
A mixture of nitric and acetic acids or acetic anhydride is employed as a nitrating mixture. ~~XX~~

The use of acetic acid as a medium is desirable in the nitration of a side chain (Bibl.27). As we know, this kind of reaction will proceed only with dilute nitric acid and with heating, as a consequence of which the nitric acid not only nitrates of the side chain, but oxidizes ~~XX~~ it to a considerable degree. Dilution of the nitric acid by acetic acid makes possible a substantial increase in the yield of nitro compounds having the nitro group in a side chain, without the need for resort to increasing

17 temperature.

It is held that in nitration with nitric acid salts in acetic acid as medium, it is possible to obtain only one of the possible isomers, whereas if sulfuric acid is the medium used, a mixture of isomers results. This assertion is based in part upon the fact that nitric acid salts are employed to nitrate, in an acetic acid medium, only those benzene ~~XXXX~~ derivatives having in their rings substitute groups which send the nitro group into the ortho or para position. When a nitro group is oriented in the meta position, nitration does not occur (Bibl.17).

In some cases it is more desirable to employ ~~XXXX~~ ^{acetic} anhydride, which also acts as a water absorbent, instead of ~~XXXX~~ ^{acetic} acid. In addition, ~~XXXX~~ ^{acetic} anhydride reacts with nitric acid, converting it into acetyl nitrate (Bibl.28) in accordance with the reactions



18 As was demonstrated by A.I. Titov (Bibl.29), ~~XXXX~~ ^{acetic} acid also reacts with nitric acid, yielding a compound of low stability*: $\text{HNO}_3 \cdot \text{CH}_3\text{COOH}$.

It is stated that the nitration mechanism when this method ^{is} employed is unique, i.e., that acetylation occurs first, and is then only followed by nitration (Bib.33).

It has also been suggested that ~~XX~~ nitration be performed with a mixture of nitric

*It should be borne in mind that ~~XXXX~~ ^{acetic} acid and acetic anhydride, when heated, are themselves ^{subject} ~~XXXX~~ to the influence of very strong (95%) nitric acid. Acetic anhydride may also serve as a good initial substance for the production of tetranitromethane (Bibl.30, 31), and the last may serve as a nitrating substance (Bibl.32).

acid and trifluoroacetic anhydride (Bibl.34).

Section 5. Nitration in the Presence of an Inert Solvent

An inert solvent (one that does not react with the reacting component) is best used if the reacting substances do not dissolve in each other. It goes without saying that the solvent must be one in which the initial substances will dissolve and, if possible, in which the reaction product will not. The use of an inert solvent, in this case, will make it possible to run the reaction in homogeneous conditions, in which it will go more readily (at a higher rate) thanks to maximum concentration of reacting substances in the sphere of reaction. Under heterogeneous conditions, the reacting substances will either be in different layers, or will be only partially distributed into each other.

In choosing an inert solvent, it should be borne in mind that certain solvents, which clearly do not react with the dissolved substance, are nevertheless capable of forming addition products of low stability with them (solvates), and this may also effect the course of the reaction itself. Successful selection of a given inert solvent frequently is of major significance to achievement of the most ^{favorable} results.

If we vary the amount of solvent, we are able to regulate the reaction rate, inasmuch as ^{an} increase in dilution reduces the concentration of the reacting components per unit volume. This is made use of, not infrequently, in nitrating substances which react with the nitrating agent at high velocity, thus making difficult control of the reaction) and ~~which~~ ^{may} lead to sudden changes in temperature when the reaction does take place (Bibl.35).

In laboratory practice, there are many solvents that may be used. However, in

18 industrial practice, it is dichloroethane and acetic acid that are employed as solvents.

Section 6. Nitration by Organic Nitrates

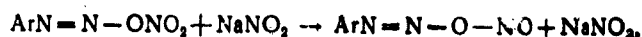
Organic nitrates: ethyl nitrates, benzoyl nitrates, and others are weak in nitrating action, but do not cause oxidation. Therefore, they may be employed for the nitration of highly ~~oxidizable~~ oxidizable substances, such as the amines (Bibl.36). Thus, ethyl nitrate will quietly nitrate anilines to mononitroaniline. In the presence of aluminum chloride, the process goes more vigorously. Benzoyl nitrate in carbontetrachloride or chloroform solution nitrates benzene, toluene, and mesitylene to their mononitro derivatives (Bibl.37). In all cases, the yield of ortho-isomer predominates. Consequently, benzoyl nitrate permits the production of the ortho-nitro derivatives even in cases in which the para isomers are the major yield when other methods are employed (Bibl.38). In reaction between benzoyl nitrate and polyalkyl-substituted benzene derivatives, the nitro group, under certain circumstances, enters not the ring, but a side chain (Bibl.39).

Acetylnitrate is a more vigorous nitrating medium (Bibl.40, 41). Its advantage over benzoyl nitrate lies in the fact that it is easier to produce and, ^{the} moreover, acetic acid results instead of benzoic acid which is difficult to remove. Acetylnitrate readily converts benzene, toluene, benzyl chloride, benzoic acids, phenol, anisole, naphthalene into their mononitro derivatives, to virtually theoretical yield (Bibl.31, 40).

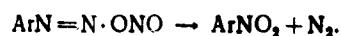
19 Section 7. Producing Nitro Compounds by Substitution of the Sulfo-, Amino-, or Diazo Groups by Nitro Groups

The sulfo-, amino-, or diazo groups may be replaced, rather readily, by a nitro group. This method of introducing the nitro group is of major significance. For example, if it is necessary to add to the first nitro group, a second in the ortho or para position,

resort is had first to producing the amino⁴ or diazo derivative, and then to ~~XXX~~ replacement ~~XXXXXX~~ of these groups ~~XXXX~~ by a nitro group in accordance with the method of Sandmeyer (Bibl.42) by mixing a neutral solution of diazonium nitrate (if an amino group were present at the outset, diazotization is first performed) with an equivalent amount of sodium nitrite. Subsequent mixture with pulverized cuprous oxide in suspension results in the ~~XX~~ formation of ~~X~~ the nitro derivative. Under this reaction, the diazonium nitrite is first formed:



which converts into the nitro compound:



The replacement of the sulfo group by the nitro group occurs by treatment of the sulfo derivatives with nitric acid. This reaction is of major significance in production of the polynitrophenol derivatives. Under specific circumstances, nitration by this method proceeds without significant oxidizing processes. Thus, for example, certain phenolsulfo acids, which in the majority of cases are readily produced from phenols and concentrated ~~XX~~ sulfuric acids, are capable of being transformed by nitric acid into nitrophenols. When phenol is nitrated by this method, it is easiest of all to replace the sulfo ~~KX~~ group in the para position relative to the hydroxyl (Bibl.43). This method is employed in producing picric acid (Bibl.44) and a number of other products (Bibl.45).

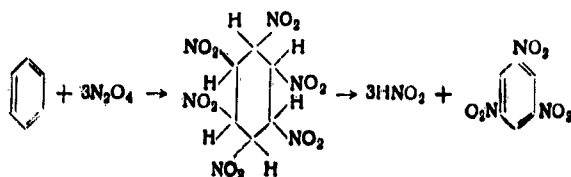
Acids of nitrogen may be employed to replace the sulfo group by nitro group (Bibl.46).

A number of other groups, such as the carboxyl, may be replaced by the nitro group (Bibl.47).

Section 8. Nitration by Nitrogen Acids (Bibl.48)

From the time ~~that~~ ^{of first} the synthetic method of producing nitric acid from nitric oxide, obtained in the process of contact oxidation of ammonium followed by oxidation of the oxide to nitrogen dioxide, chemists ~~XXXXXXXXXX~~ were attracted by the possibility of employing ~~XXXXXXXXXX~~ in nitration, not the nitric acid as such, but the intermediate product produced in the synthesis thereof - nitrogen dioxide. Numerous ~~XXX~~ studies in this direction demonstrated the relatively low practicality of nitration of aromatic compounds by nitrogen oxides. This reaction may still have some significance in nitration of aliphatic hydrocarbons; The investigations determined that, among the aromatic compounds, the phenols and amines react readily with nitrogen dioxide, yielding primarily mononitro derivatives. Benzene does not react in the cold with nitrogen dioxide, but upon heating, this reaction goes partially in the direction of production of trinitrobenzene and nitrobenzene, and partially in the direction of oxidation, accompanied by the ~~XXXXXXXXXX~~ formation of trinitrophenol, carbonic, and oxalic acids.

This reaction was discovered by Wieland, and he ascribes the following equation thereto (Bibl.49). At the site of the double bonds, there proceeds attachment, simultaneously, of six NO₂ groups, followed by decomposition of the resulting hexanitrocyclohexane into three molecules of nitrous acid and trinitrobenzene:

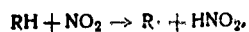


Only then is the trinitrobenzene oxidized to picric acid.

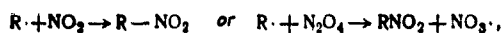
In his experiments in the nitration of toluene with ~~XXXXX~~ nitrogen acids, A.I. Titov

discovered a difference in the direction taken by the reaction depending upon ~~XXX~~ whether the monomeric or dimeric form of nitrogen dioxide was acting upon the toluene. It was found that when the nitrogen dioxide was highly diluted by toluene (raising the degree of dissociation $N_2O_4 \rightleftharpoons 2NO_2$), the yield of nitrotoluenes was sharply reduced, with a simultaneous increase in the amount of nitration products in the side chain. Saturation ~~XX~~ ^{by} a mixture of ~~XXX~~ chlorine (Bibl.50) or oxygen greatly accelerates the reaction (Bibl.51).

The fact that the monomeric form of nitrogen dioxide is similar to the radical made it possible for A.I.Titov to suggest that free radicals also appear in the compound being nitrated:



and, further, that the reaction of the radical with nitrogen dioxide must lead to the formation of nitro compounds:



where NO_2 is the active molecule.

The nitration ~~XX~~ of aromatic compounds by nitrogen dioxide in the presence of aluminum chloride and ferric chloride (Bibl.48, 52, 53) proceeds through a stage of formation of stable complex. Water decomposes the resulting compound, and the organic residue $C_6H_6 \cdot N_2O_4$, splitting off HNO_2 , converts to nitrobenzene.

A.I.Titov (Bibl.54) determined that this reaction proceeds stepwise.

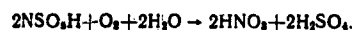
Sulfuric acid (Bibl.55) or boron fluoride (Bibl.56) may be employed as activator of the aromatic ring in nitration by nitrogen oxides. When nitrogen oxides are introduced into a mixture of sulfuric oxide and hydrocarbon, complete absorption,

20 of the oxides occurs. In nitration, only 50% of the nitrogen oxides are employed, the other half undergoing reaction with the H_2SO_4 , to form nitrosyl sulfuric acid:



The desirability of utilizing this reaction depends upon successful solution of the problem of recovering the 50% of the nitrogen dioxide which is incorporated into the nitrosyl sulfuric acid.

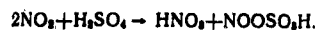
Battegay (Bibl.57) suggests that this may be done by oxidizing the nitrosyl sulfuric acid in accordance with the reaction



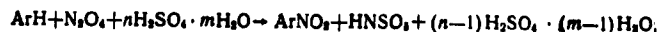
According to A.I. Titov, ~~the~~ ^{this} same objective may be achieved by adding salts of persulfuric acid to the reaction mixture after the first reaction phase (Bibl.54):



N.N. Vorozhtsov holds that the process of nitration of nitrogen dioxide in the presence of sulfuric acid proceeds due to the nitric acid formed as a consequence of reaction between nitrogen dioxide and sulfuric acid:



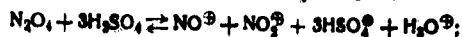
A.I. Titov ~~XXXX~~ agrees with this, but offers a somewhat different reaction equation:



thus emphasizing the profound relationship between the nitration reaction and the process of saturation of the force field (the coordination field) of ~~XXXX~~ sulfuric acid by elements of nitric acid and water.

21 It has now been determined, with the aid of Rayman spectra (Bibl.58) that the following ions exist in sulfuric acid solutions of nitrous anhydride, nitrogen dioxide,

and nitric anhydride:



of which the NO_2^+ ~~XXXXXXXXXXXX~~ are the ions of the active nitrating agents.

It has been remarked that when nitric oxides are employed as the nitrating agent without additives, there is a change in the orientation of the nitro group introduced when compared to its ~~XXXXXXXX~~ orientation when nitric acid is the agent employed (Bibl.59, 60).

Section 9. Nitration in the Presence of Catalysts

The first studies connected to the discovery of catalysts for the nitration reaction go back to the beginning of the present century. In 1901, M.I.Konovalov (Bibl.61) found that the addition of a small amount of potassium nitrite to the reaction solutions facilitated the reaction. Subsequently, A.I.Titov (see, below, "the Nitric Acid Nitration Mechanism") demonstrated that this phenomenon relates to the fact that weak nitric acid (M.I.Konovalov used weak acid) will nitrate only in the presence of nitrogen oxides, which are added, in the given instance, in the form of KNO_2 .

It was noted that boron fluoride had a ~~XXXX~~ catalytic effect upon the nitration reaction rates (Bibl.15). A detailed investigation ~~XXXXXXXX~~ showed that this substance is simultaneously a water absorbent, and that this also facilitates the nitration reaction (Bibl.18, 19). It was found that when nitration of benzene and toluene by nitrogen dioxide was performed in the gaseous condition, silica gel was the best of the various catalysts (Bibl.62). However, this catalyst is quite weak in its action.

21 The reaction proceeds only to the formation of the mononitro compound.

Mercury nitrate has a strong influence upon the nitration process. This was first determined by Holdermann with respect to anthroquinone (Bibl.63), and was later verified with respect to the ~~XXXXXXXX~~ nitration of a number of substances: benzene (Bibl.64), toluene (Bibl.65), naphthalene (Bibl.66), benzoic acid (Bibl.67), and others (Bibl.68).

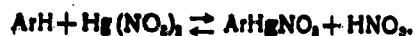
Wolffenstein and Boters (Bibl.64) observed that when moderate-strength nitric acid reacted with benzene in the presence of a mercury salt, a considerable quantity of nitrogen oxides was released. Investigating this phenomenon they found that the major reaction products are oxynitro compounds: dinitro- and trinitrophenol and ~~XX~~ nitrobenzene in small quantities. They discovered that the reaction depends upon the strength of the nitric acid: strong nitric acid (or mixed nitric and sulfuric acid) yields only nitrobenzene in the presence of a mercury salt. When dilute nitric acid is used, the amount of nitrobenzene formed diminishes, but there is a simultaneous increase in the quantity of nitrophenols formed.

Addition of a mercury catalyst yields no oxidizing effect in cases of nitration of aromatic compounds containing nitro groups (Bibl.69). Nitration of nitric acid in the presence of mercury, leading to the formation of nitroxy compounds is termed oxidizing nitration. The oxidizing nitration of benzene to dinitrophenol has been elaborated, and may be introduced into industry (Bibl.70, 71, 72, 73).

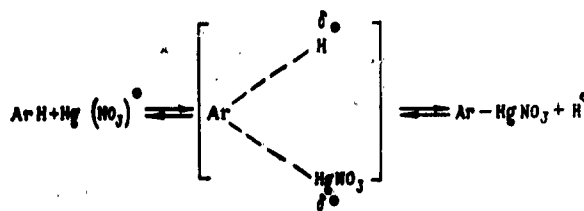
The significance of mercury in oxidizing nitration has been clarified by studies due to ~~XX~~ A.I.Titov and N.G.Laptev (Bibl.70, 71), Westheimer (Bibl.74), Kermack (Bibl.73). They proved that the mercury nitrate in the reaction mass reacts with the

compound undergoing nitration, to form a mixed organic mercury compound -

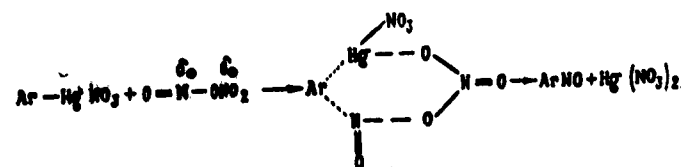
arylmercuronitrate:



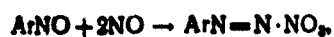
With increase in the strength of the nitric acid, the depth of mercurization diminishes. In the absence of nitrogen oxides, the reaction goes no further. The organic mercury compound reacts with the nitric acid, recovering the initial hydrocarbon (until equilibrium is established). The mechanism of mercurization, according to A.I. Titov (Bibl. 70, 71) may be expressed by the following diagram:



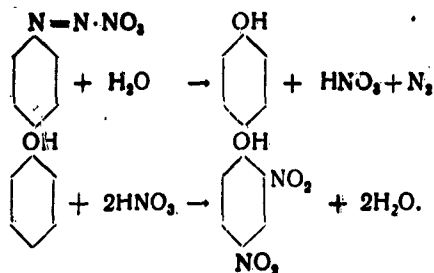
In nitric acids containing nitrogen oxides, the organic mercury compound rapidly reacts further to form nitroso compounds. It is most probable, according to A.I. Titov and N.G. Laptev that the action occurring is that of the nitrosyl-nitrate form N_2O_4 , in accordance with the following equation:



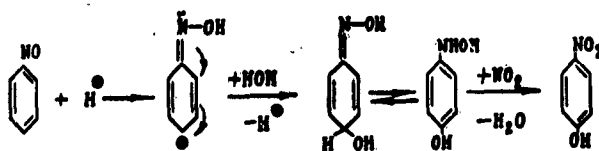
Nitroso compounds in nitric acid containing nitrogen oxides can convert to oxynitroso compounds by two different paths. Ten percent is converted via the diazo compounds:



which decompose to form the oxy compounds, which are readily nitrated to the nitrophenols by dilute nitric acid:



90% of the nitroso compound converts to nitrosophenols which are then oxidized to nitrophenols:



The slowest reaction determining the rate of the process is the formation of benzene benzolmercuronitrate. The rate of catalytic nitration of the ~~benzene~~ increases markedly with rise in the concentration of acid (for example, when the HNO_3 rises from 47.5 to 60%, the rate multiplies sevenfold). This is due to the increase in the solubility of the benzene and to an increase in the activity of the mercury ion due to the reduction in the degree of its hydration (Bibl.74).

In one of his papers (Bibl.75), A.I.Titov demonstrated, using the oxynitration of toluene as example, that the relationship of the reaction speeds of transformation of nitroso compounds in the two directions depends upon the nature of the nitroso compound and the composition of the reaction medium. Conversion of nitroso compounds into para-oxyhydroxylamine is favored by increase in the strength of the acid and increase in temperature. ~~XXXX~~ Increase in the strength of the NO has the contrary effect of

23 accelerating conversion of the nitroso compounds into diazo compounds.

Section 10. Nitration by Nitric Acid, with the Water Driven Off

A significant shortcoming of the most common method of nitration is the need to make use of sulfuric acid. Recovery of the ~~XXX~~ sulfuric acid from the spent material which contains not only water but nitrogen compounds and organic substances requires special equipment and expenditure of heat.

Recently, a number of suggestions have appeared (Bibl.76) envisaging nitration by nitric acid without the use of sulfuric acid. Elimination of the water formed in the reaction is by steaming in the form of an azeotropic mixture with an excess of the compound being nitrated, or a specially added solvent (inert relative to nitric acid).

Many hydrocarbons form azeotropic mixtures with water. Thus, benzene and water forms a ~~XXXXXXX~~ mixture that boils at 69° , whereas toluene forms one that boils at 84.1° . At the same time, the boiling points of the individual compounds are substantially higher. The boiling point of benzene is 80.4° , that of toluene is 110.8° . If the temperature in the reactors is held equal to the boiling point of the ~~XXX~~ azeotrope, the water formed in the process of the nitration reaction may be eliminated. An advantage of this method is the fact that it does not result in spent acid and consequently there is no need to recover the latter.

Under this method, the water vapor entrains a considerable quantity of nitric acid. To eliminate this, and to return the hydrocarbon, a fractionating column is employed. As the difference in boiling points is great, only a small number of theoretical plates is required for distillation at atmospheric pressure.

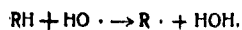
To separate the continually boiling mixture, ~~XXX~~ an intermediate settling tank is provided. In this tank, the hydrocarbon and water layer out and the hydrocarbon may

then be reused for nitration. Thus, if the rate of nitration is controlled by the rate of removal of the water formed, the type of column used makes it possible to maintain the required strength of the nitric acid. Under these conditions, nitration performed is ~~XXXX~~ with the minimum quantity of nitric acid. Nitration proceeds at a greater rate when gaseous nitric acid is employed, the vapors of which, diffusing into the hydrocarbon, make for greater homogeneity in the mass and the maximum reactant surface contact.

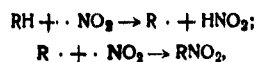
In the opinions of certain scientists, nitric acid in the vapor phase has stronger nitrating effects than in other forms (Bibl.77). The decomposition of nitric acid at high ~~KX~~ temperature has not been studied in detail. All that is known is that the formation ~~XX~~ of the following occur: NO_2 , NO , O_2 , and H_2O . However, apparently nitric acid also dissociates in accordance with the scheme



The hydroxyl radical formed in this procedure converts the hydrocarbon into an alkyl or aryl radical:



The NO_2 radical also reacts with the hydrocarbon:



and the reaction consists of the attachment of two different radicals, in which an electron pair is formed (Bibl.77).

The advantage of this type of nitration, in addition to elimination of the consumption of sulfuric acid and the need to recover it, is the absence of cooling, and high rate of output. The process lends itself readily to continuous-flow

production. A shortcoming is the need to employ quality stainless steel.

The water of reaction, in the form of an ~~XX~~ azeotropic ~~MIXTURE~~ mixture, may be driven off in the nitration of benzene and in the presence of sulfuric acid, the sole difference being that the distillation must be performed in vacuo. At the end of the nitration process, one obtains nitrobenzene and sulfuric acid (in a strength equal to the initial strength), ready for reuse.

It must be borne in mind that if dilution is adequate and temperature high (over 100°), aqueous nitric acid reacts not with the aromatic ring, but upon the side chain ^{the} (according to M.I. Kononov reaction). Therefore, in the nitration of high-boiling-point substances (naphthalene, nitrobenzene, etc.), the water may be driven off in the form of an azeotropic mixture with a specially added diluent, such as low-boiling petroleum hydrocarbons, to avoid having to conduct the nitration at high temperature.

A number of other methods of introducing the nitro groups are known, but they do not have practical significance for the production of explosives of the nitro derivatives class.

Of all the methods of introduction of the nitro group listed above, only four are of practical significance in explosive synthesis: nitration by mixed acids, nitration by pure nitric acid or in a medium of acetic acid in the presence of acetic anhydride, and substitution of a nitro group for the sulfo group. The method of nitration with driving off of the water, and nitration in the presence of mercury nitrate also offer possibilities.

B. The Mechanism of Nitration

Summary chemical equations do not refer to the actual course of chemical reactions,

24 but describe only the initial and terminal condition of the system. A study of the actual course of the chemical processes observed, and of their mechanism, is of interest not merely as a matter of knowledge, but in practical terms, because it makes it possible to find means for increasing the rate and the yield of the required products.

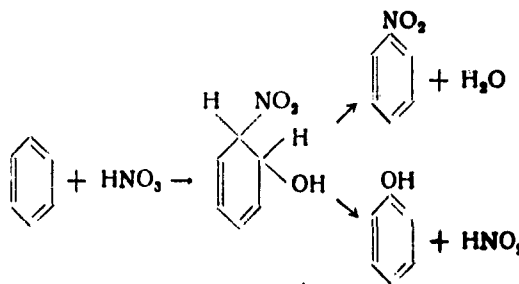
A theoretical investigation of the nitration process may, to a considerable degree, assist in solving a number of technological problems and may provide the means for controlling these problems in terms of considerations of economy and safety in manufacture.

Over a long period of time, the aromatic ~~compounds to nitration process~~ ^{nitration} mechanism of nitration of aromatic ~~compounds~~ as well as that of other substitution reactions, was studied without consideration of the structure of the reacting components or of the reactions and equilibria preceding nitration.

Only during the past 10 - 12 years ~~has~~ ^{has} the study of these reactions made it possible to set up a rigorous picture of the nitration mechanism, which provides a satisfactory explanation for the factual data observed in the investigation of this process.

Section 1. Mechanism of Nitration by Nitric Acid

In 1837, Armstrong offered the suggestion that the nitration reaction passes through an intermediate stage - the attachment of nitric acid to a double bond in the aromatic compound:



A more detailed elaboration of this theory was performed by Hollemann, and

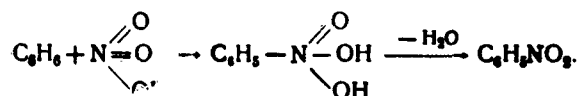
subsequently by Wieland (Bibl.78), who attempted to classify the additional products of nitric acid with the unsaturated hydrocarbons, naphthalene, and anthracene.

S.S.Nametkin (Bibl.79) and B.V.Tronov (Bibl.80) have taken exception to the Armstrong-

Wieland nitration mechanism, holding, justifiably, that the supposed intermediate

product - the ~~nitro alcohol~~ ^{nitro alcohol} - tends to various oxidation reactions and, to a lesser degree, to decomposition into an aromatic nitro compound and water. Therefore, the smooth conversion of an unsaturated ~~nitro alcohol~~ nitro alcohol into nitrobenzene is improbable for all practical purposes. Later researchers have demonstrated the erroneousness of the experimental data upon which the ~~nitro alcohol~~ Armstrong-Wieland nitration mechanism rested (Bibl.81, 82, 83 and others).

S.S.Nametkin (Bibl.79) suggested that nitration goes through formation of an intermediate product by addition of the hydrocarbon to the nitric acid as follows:



In this case, the intermediate product retains its aromatic nature.

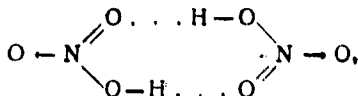
B.V.Tronov (Bibl.80) offered the hypothesis, by way of supplementation of this mechanism, that two molecules of nitric acid, possibly in a complex, participate in the reaction. A.V.Topchiyev confirmed the correctness of the experimental results of B.V.Tronov by a series of studies in the nitration of aromatic compounds by nitric acid and its salts in the presence of complex forms (Bibl.84).

The authors

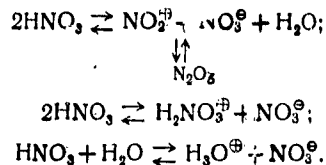
~~of these studies~~ built the nitration mechanism on the assumption that the process is participated in by molecules of nitric acid, and left out of consideration the possibility of conversion thereof under the influence of the medium in which the

25 reaction occurs.

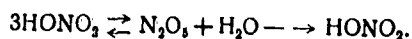
'Study of the physical-chemical properties of nitric acid shows that, depending upon its strength, it may take various forms: either neutral molecules HONO_2 (anhydrous nitric acid), which may partially be transformed as a consequence of hydrogen bonds in
26 the dimer (Bibl.85,86):



or in the form of ions formed according to the following equation (Bibl.87, 88, 89, 90, 91, 92):



The reaction whereby N_2O_5 and NO_2^{\oplus} are converted into HNO_3 is associated, in terms of energy, to the process of solvation of water and of each of the ions by one or two molecules of nitric acid, by such processes as (Bibl.83, 93):



Anhydrous nitric acid contains about 8% molar dissociation products (Bibl.89). Upon addition of the water, the nitric acid forms unionized complexes of the following composition: $(\text{H}_2\text{O}) \cdot (\text{HNO}_3)_2$ and $(\text{H}_2\text{O}) \cdot (\text{HNO}_3)$, which appear as a result of the hydrogen bonds $(\text{H}_3\text{O})^{\oplus} \cdot (\text{NO}_3)^{\ominus}$. The equilibrium in the reaction whereby nitric acid dissociates into solutions containing little water:

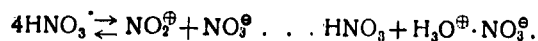


is displaced in the direction of the undissociated acid, the content of which in

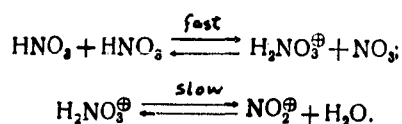
26 dilute 48% HNO₃ is estimated at from 5 - 10%. The more dilute solutions are almost entirely dissociated (Bibl.86). The degree of dissociation diminishes with increase in temperature (Bibl.90).

Ingold (Bibl.87, 94), and Millen (Bibl.95) advanced the suggestion that in an aqueous nitric acid solution, the nitrating substance is the H₂NO₃[⊕] ions. An analogous point of view had been put forth previously by Usanovich (Bibl.96), who based his work upon that of Hantsch (Bibl.97), who believed possible the reaction between two molecules of nitric acid, in which one HNO₃ molecule plays its normal role of acid, and the other functions as a base.

The work of A.I.Titov (Bibl.83, 98), as well as the subsequent studies due to Ingold (Bibl.99, 100, 101) showed that the self-ionization of nitric acid leads to the formation not of the H₂NO₃[⊕] and H₃NO₃^{⊕⊕} cations, but to the formation of the NO₂[⊕] cation in accordance with Titov's scheme.



In accordance with Ingold, ionization proceeds through formation of the nitracidium ion:



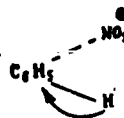
It was found (Bibl.93) that the solid nitric anhydride has the following ion structure [NO₂][⊕] · [NO₃][⊖], whereas, in anhydrous nitric acid, a temperature of -40°,

27 3.4% of the substance undergoes dissociation, forming 1.2% of the nitronium ion (NO₂)[⊕], 1.7% of the nitrate ion (NO₃)[⊖] and 0.5% water. Upon addition of water, the concentration of NO₂[⊕] drops rapidly, and reaches zero, for all practical purposes,

at 5 - 8% H₂O (Bibl.93,95).

An investigation of perchlorate nitracidium [H₃NO₃][⊕] · [ClO₄]₂[⊖], identified by Hantsch showed that this salt is a mixture of nitronium perchlorate (nitryl) [NO₂][⊕] · [ClO₄][⊖] and hydroxonium perchlorate [H₃O][⊕] · [ClO₄][⊖] (Bibl.101). This confirmed the fact that the positively charged ions of nitric acid do not have the structure H₂NO₃[⊕] and H₃NO₃[⊕], but NO₂[⊕].

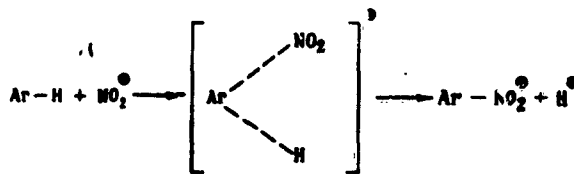
A.I.Titov (Bibl.83, 98, 102, 103, 104, 105, 106) demonstrated, in a large group of aromatic compounds (phenol, its homologs, naphthalene, benzene, toluene, etc.) that the formation of the nitro derivatives in strong nitric acid proceeds via the reaction of molecules of the aromatic compound with the nitronium cation O = N = O, yielding transitional complexes of the type



thanks to the presence of a nitrogen atom ~~XXXX~~ unsaturated in terms of coordination.

He termed this type of process, constituting replacement of hydrogen by the nitro group

by the following procedure



^{known as}
normal nitration (Bibl.98).

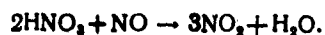
As the formation of NO₂[⊕] proceeds by a reversible reaction of at least the fifth order, its concentration in the HNO₃ solution is low, as a consequence of which the rate of nitration is highly dependent upon the strength of the nitric acid. Therefore,

although the gain in energy in formation of the transition complex is of the required magnitude:



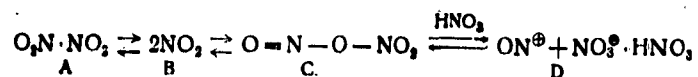
compounds of the type of nitrobenzene are capable of being nitrated to any significant degree only by strong nitric acid, due to the very low ~~XXXXXXXXXX~~ potential of the electron ~~ME~~ in NO_2^{\oplus} . Acid of medium strength will nitrate even active aromatic compounds only at low velocity.

The nitration of dilute ~~XXXXXXXXXX~~ nitric acid (specific gravity 1.4 or less), not containing the NO_2^{\oplus} cation, proceeds only in the presence of nitric oxides, by reaction between aromatic compounds with various forms of nitrogen dioxide (Bibl.107). A.I. Titov calls this type of nitration catalytic (Bibl.98, 105). In this situation, the molecules of nitric acid serve as the source of nitrogen dioxide in accordance with the following procedure



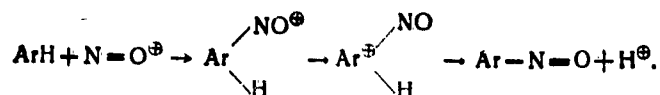
Side processes of oxidation result in an increase in the strength of the nitric oxides in the nitration process.

A.I. Titov examines the reaction mechanism with consideration of the influence of the medium and other factors upon the equilibrium of various forms of nitrogen dioxide:



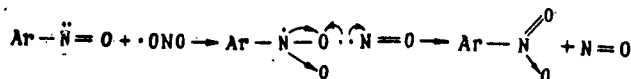
In a polar medium, the oxides have form ~~D~~ D, and in non-polarized, their forms are those shown as A and B. If the acid is strong enough (a polar medium), and if the temperatures are low and the concentrations of nitrogen oxides are low, the aromatic

compound will react with the nitrosyl cation:

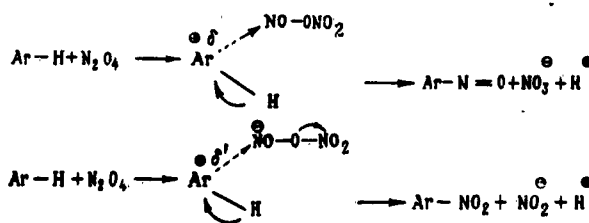


Dilution by water reduces the rate of catalytic nitration by suppressing the dissociative effect of nitric acid upon N_2O_4 . An analogous (but stronger) effect is caused by the addition of nitrates (Bibl.108). Titov states that the activity of the nitrosyl cation must necessarily increase with increase in the acidity of the medium, and diminish in solvents basic in nature, due to formation of complexes of the type $\text{O}=\text{N}^{\oplus} \leftarrow \text{OR}_2$, in which the ~~electrophilic~~ ^{electrophilic} nature of the nitrogen will be diminished.

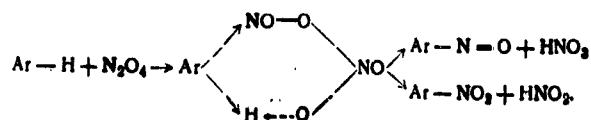
The conversion of nitroso compounds into nitro compounds also proceeds only in the presence of nitrogen oxides (Bibl.71, 83, 98) as follows:



In an unpolarized medium, ~~XX~~ reaction with N_2O_4 and NO_2 results in the formation ~~XX~~ not only of the nitroso compounds converted, at a second stage, into nitro compounds, but also in direct formation of nitro compounds:



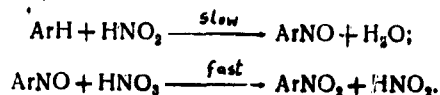
When the medium is of low polarity, the reaction has to pass through a cyclic modification of the transition complex (Bibl.83):



Direct oxidation of the nitroso ~~XX~~ group to the nitro group at the instant it appears is facilitated when the $\text{ArH}(\delta' > \delta)$ is a good electron donor. This is evident from the example of catalytic nitration of phenol and naphthalene by nitric acid. The nitration products of these chemicals are virtually lacking in nitroso compounds.

Under the conditions of nitration, nitroso compounds are also subject to other transformations (Bibl.71, 83), the most important of which are the formation of oxynitro compounds and diazo compounds.

The increased ~~XXXXXXXX~~ rate of nitration of phenol, aniline, and their derivatives, upon addition of nitrogen oxides to the nitric acid, as brought about by Ingold, and others (Bibl.99, 107, 109), is also explained by the participation of nitrogen oxides in the nitration reaction in the form of the nitrosonium ion (NO^+). They contend that the reaction proceeds in two stages: first with formation of the nitroso compound, which then rapidly undergoes oxidation by nitric acid into the nitro compound. As this occurs, the HNO_3 converts to HNO_2 , which is ~~XXXXXXXX~~ needed for the first and slow stage of the reaction:



The scheme envisaged by A.I. Titov is also confirmed by the work of the late Blackwell (Bibl.108), who studied the kinetics of nitration of para-chloranisole by nitric acid in an acetic acid medium. The process was apparently catalyzed by nitrogen oxides, on the basis of which it was demonstrated that, under these conditions, the nitrating agent is the nitrosonium ion (NO^+) and a molecule of the dimer of nitrogen dioxide (N_2O_4). It is found that the ~~XXXXX~~ ^{former} operates ten times as rapidly as the latter.

The ~~critical~~ interval of concentration of nitric acid in which the transition from the catalytic reaction to normal nitration occurs, is determined by the nature of the aromatic compound, the concentrations of nitrogen acids, and the temperature. Very active aromatic compounds of the type of naphthalene are nitrated by a catalytic mechanism at high speed and to high acid strength (up to 80% HNO₃). Aromatic compounds of ^{medium} activity (such as benzene) are nitrated by nitrogen oxides at a very low velocity and only by very weak nitric acid (10 - 20% HNO₃) (Bibl.105).

The nitrosyl cation and the electron NO₂, of the same order of potential, and NO-ONO₂, are considerably less ~~electrophilic~~ ^{electrophilic} than the nitronium cation O = N⁺ = O. Therefore, it is only compounds having high electron donor ~~AAA~~ capacities (Bibl.83), whose relative electron potentials are 0.1 or more (naphthalene, anthracene, the amines, and the phenols) that are capable of rapid nitration through intermediate reaction with these oxides. Entry into the ring of substitute groups such as the nitro group must strongly reduce the potential of the electron and correspondingly reduce the rate of nitration via the catalytic mechanism.

With increase in the strength of the nitric acid, the accelerating effect of the nitrogen oxides ceases to be manifested, and the nitro derivatives content of the reaction product increases. These nitro derivatives are formed by the NO₂⁺ cation, i.e., without participation of nitrogen dioxide (Bibl.104, 105).

The rate of nitration by the nitronium cation is, because of its high activity, substantially less dependent upon the polarizability of the aromatic compounds.

Dilute nitric acid, not containing nitrogen oxides, is not capable of nitrating even such readily nitratable compounds as naphthalene.

The theoretical hypotheses were verified by A.I. Titov, experimentally, upon a number of products. When nitric acid of 1.4 specific gravity was employed to treat naphthalene in the presence of nitrogen ~~oxides,~~ ^{oxides,} mononitronaphthalene ~~was formed~~ ^{was formed} within a few minutes. When nitric acid was employed under the same experimental conditions, but without nitrogen oxides, the naphthalene remained unchanged (Bibl.82).

In work by Bunton (Bibl.110, 111) on exchange between the heavy hydrogen in water with HNO_3 and on the ~~nitration~~ nitration of toluene, nitrophenol, and other aromatic compounds by aqueous (70 - 85%) nitric acid at 0°C temperature, it was shown that in aqueous nitric acid of lower than 70% strength, an exchange between heavy hydrogen and HNO_3 proceeds only in the presence of nitrogen dioxide. At greater strength than this, the exchange occurs in the absence of nitrogen oxides. As the strength of the nitric acid increases, the reaction rate ~~shows~~ ^{Comparison} shows a rapid rise. ~~Comparison~~ of the rate of nitration with the rate of oxygen exchange reveals that the rate of nitration approximates the rate of exchange (Bibl.111).

On the basis of the foregoing, the authors contend that, in dilute nitric acid, nitration proceeds through nitrogen oxides, whereas in strong nitric acid, the nitrating agent is the nitronium ion.

Recently, the processes of ~~nitration~~ nitration of aromatic compounds by nitric acid have been the object not only of theoretical studies but have acquired broad practical significance. Nitration by nitric acid on an ~~industrial~~ industrial scale is performed either with excess nitric acid, or with removal of the water formed by driving it off as an azeotropic mixture with the substance being ~~nitration~~ nitrated, or,

diluent
by a specially added ~~EXCESS~~ (Bibl.112). Nitration in the vapor phase has
also been suggested (Bibl.113).

dissolve compounds
The high capacity of nitric acid to ~~EXCESS~~ the majority of organic ~~EXCESS~~
makes it possible to perform nitration under homogenous conditions. Increased
reaction velocity should be facilitated by the large modulus of the nitration bath,
~~EXCESS~~ and the good solubility of the initial product in acid. Upon nitration by
dilute nitric acid, nitrogen oxides should be present in the latter .

Section 2. Kinetics of Nitration by Nitric Acid

Nitration by nitric acid alone proceeds with the use of a considerable excess
thereof over the theoretical. This is due to the need to eliminate the influence of
dilution of the acid by the water liberated in the course of the reaction.

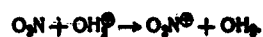
and
An investigation of the kinetics of nitration of benzene, toluene, /ethylene benzene,
under similar circumstances (5 moles of nitric acid per 0.1 mole of the compound
being nitrated) has shown that the nitration velocity remains unchanged until all
the substance being nitrated has undergone reaction. Consequently, the reaction is
of zero order. The nitration velocity ~~EXCESS~~ constants of benzene, toluene, and ethyl benzene
are identical, and not dependent upon the concentration of the compound being nitrated
(Bibl.114).

Upon nitration in acetic acid or nitromethane, the order of reaction is determined
by the nature of the substance being nitrated. Nitration of aromatic compounds
~~EXCESS~~ adequately sensitive to reaction involving electrophilic substitution ~~EXCESS~~ proceeds
at virtually identical velocities and in the zeroth order, whereas in the case of
substances having low capacity to react to this substitution, it is of the first

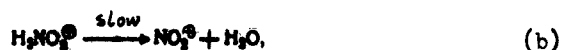
order (Bibl.99).

Nitration of aromatic compounds by ~~IX~~ nitric acid, particularly in organic solvents, is accelerated by additions of sulfuric acid and inhibited by additions of metals and water, which dissociate nitrates. Additions of the latter not only diminish the velocity, but in some cases change the order of reaction (from the zeroth to the first).

On the basis of these facts, ^{Ingold} ~~XXXXXX~~ (Bibl.99) assumes that the velocity of nitration depends upon the preliminary process influenced by the solvent. He ~~XXXXXXXX~~ considers this process to be the formation of the nitronium cation by disruption of the bond in the ~~XXXXX~~ Hantsch cation:



The hypothesis that NO_2^\oplus is formed from $\text{H}_2\text{NO}_3^\oplus$ is based upon the fact that the nitration velocity increases upon addition of the stronger acids (H_2SO_4), which facilitate conversion of HNO_3 and $\text{H}_2\text{NO}_3^\oplus$. Thus, a proton joining the molecule of nitric acid, is supplied either by the nitric acid itself:

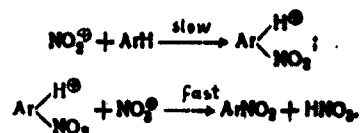


or by the stronger acid (H_2SO_4):



31

The second process in nitration due to Ingold is the process of reaction between the nitronium cation NO_2^\oplus with the aromatic compound undergoing nitration:

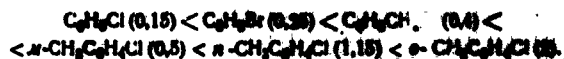


If the latter reacts weakly, the total reaction speed is governed by the velocity of this particular process, and the order becomes first-order in terms of the compound undergoing nitration. The velocity constant of the first order depends upon the nature of the compound undergoing nitration. However, if the compound to be nitrated is of high reactivity, it will react with the nitronium cation more rapidly than the composition of H_2NO_3^+ occurs. Therefore, in this instance, the reaction velocity constant does not depend upon the nature of the compound being nitrated, and the reaction is of zero order.

Nitration of phenol by ~~XX~~ nitric acid in aqueous solution is a complex autocatalytic ~~XXXXXXXXXX~~ reaction (Bibl.115). Its velocity increases with increase in the strength of the acid, and diminishes with increase in the concentration of phenol. Nitrous acid is a strong positive catalyst for this reaction. In the absence of nitrous acid, ~~XXXXXXXX~~ phenol undergoes virtually no nitration by nitric acid. With nitric acid of a specific strength, the reaction velocity is directly proportional to the strength of the compound being nitrated and to the nitrous acid. With increase in the strength of the nitric acid, the rate of nitration increases sharply.

A comparative study of the kinetics of phenol nitration in an aqueous medium and in acetic acid medium has shown that the reaction velocity, given equal strength of acid, is considerably ~~XXXXXXXX~~ higher ^{an} in/acetic acid medium than in an aqueous medium.

The rate of nitration of aromatic compounds of nitric acid in acetic anhydride as medium is determined by the nature of the aromatic compound (Bibl.116) and increases in the following order (the nitration velocity of benzene is taken as unity): benzene (1), ~~meta-xylene~~ meta-xylene (7), mesitylene (25), pseudocumene (28). In the case of the halides, the sequence is as follows:



Chohen and Wibaut (Bibl.31) contend that nitration by a mixture of nitric acid and acetic anhydride proceeds through the stage of formation of a mixed anhydride - acetylnitrate (CH_3COONO_2). It is shown that under these circumstances, too, the rate of nitration is increased catalytically by nitrous acid, the effect of the latter being weakened when the particular maximum concentration thereof in the mixture is attained.

Section 3. The Mechanism of Nitration by Mixed Sulfuric and Nitric Acid

When aromatic compounds are nitrated by nitric acid, a nitro compound and water are formed:



Despite the irreversibility of this process, the water liberated diminishes the nitrating effect, as a consequence of its effect upon the state of the nitric acid, and does not permit the acid to be fully employed to form the nitro compound. Therefore, since the last Century, the process of nitration has been performed, in ~~industrial~~ industrial conditions in a sulfuric acid medium, the sulfuric acid being added for the purpose of taking up the water. However, as far back as 1899, V.V.Markovnikov (Bibl.117) observed that sulfuric acid is not only a water-removing substance, but

also serves to increase the nitrating effect of the nitric acid (the nitrating effect of an ~~XXXXXXXX~~ anhydrous mixed sulfuric and nitric acid is higher than that of anhydrous nitric acid alone). As an explanation of this ~~XXXXXXXX~~ ^{phenomenon} he hypothesized that, when sulfuric and nitric acid react, a nitro sulfuric acid is formed in accordance with the following equation



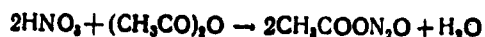
In the opinion of V.V. Markovnikov, nitro sulfuric acid has a greater tendency to substitutional reactions in nitration than does ~~XXXX~~ nitric acid



32

One proof of this analysis of the reaction mechanism was held, by him, to be the emission of much heat in the preparation of the acid mixtures from the individual ~~XX~~ components thereof. The higher nitrating effect of mixed acid than of nitric acid ~~XX~~ is evident from the fact that this mixture readily nitrates nitrobenzene to dinitrobenzene, whereas concentrated nitric acid will nitrate this product only with difficulty even upon boiling.

At present, nitric acid compounds are known whose ~~XX~~ structure is analogous to that of nitro sulfuric acid: acetylnitrate $\text{CH}_3\text{COONO}_2$ which is formed in accordance with the reaction



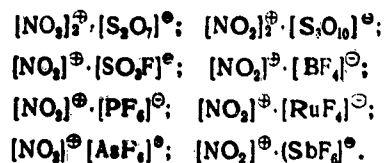
(and which has a higher nitrating effect than nitric acid) (Bibl. 31, 118, 119, 120), and a compound of nitric acid and sulfuric anhydride $\text{HNO}_3 \cdot 2\text{SO}_3$ produced in 1939 by ~~XXXXXXXXXX~~ V.V. Filipchuk, and later by others (Bibl. 121).

Spasokukotskiy (Bibl. 122) holds this compound to be an electrolyte of the following structure: $[\text{NO}_2]^{\oplus}$, $[\text{HS}_2\text{O}_7]^{\ominus}$. The accuracy of Spasokukotskiy's hypothesis

Raman

was confirmed upon study of the ~~IR~~ spectrum of this compound (Bibl.95) and determination of the melting points of a mixture of nitric acid and sulfuric anhydride (Bibl.123).

Subsequently (Bibl.124) a further series of nitric acid compounds in the NO_2^+ form was found:



physical-chemical

A.V.Sapozhnikov studied the ~~physical-chemical~~ (Bibl.125) and the nitrating (Bibl.126) properties of mixed acids and found that sulfuric acid increases the nitration velocity only up to the point at which a specific concentration of water in the acid mixture is attained. ~~Below~~ Below this concentration, the nitrating capacity of the mixture of ~~mixed~~ sulfuric and nitric acid diminishes. This interesting phenomenon; showing that sulfuric acid plays a more complex role in the nitration reaction than merely that of freeing it of water was explained by A.V.Sapozhnikov in terms of the effect of the sulfuric acid upon the condition of the nitric acid in the acid mixture. A.V.Sapozhnikov's theory of nitration has been accepted by all scientists throughout the world and has not lost its significance to this day, although ~~in~~ another scientific interpretation of it is given.

physical-chemical

A.V.Sapozhnikov's investigation of the ~~physical-chemical~~ properties of ternary mixtures $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ showed that, when nitric acid is added to sulfuric acid, the electrical conductivity increases sharply. The sulfuric acid ~~exercises~~ ^{exercises} a significant

influence upon the vapor pressure of the nitric acid. As sulfuric acid is added to the monohydrate diluted by the nitric ~~acid~~ acid, the vapor pressure increases and; attaining a maximum at a ratio of $\text{HNO}_3 + n(\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O})$, it begins to diminish. However, the vapor pressure drops not in proportion to the drop in the strength of the anhydrous nitric acid in the mixture, but somewhat more rapidly than this, i.e. as would be the case if a portion of ^{the} HNO_3 had disappeared. These observations enabled A.V.Sapozhnikov to assume that a reversible process ~~exists~~ occurs in mixed sulfuric and nitric acid:



Consequently, according to A.V.Sapozhnikov, the nitric and sulfuric acids in the ternary mixture $\text{HNO}_3\text{-H}_2\text{O-H}_2\text{SO}_4$ are found as hydrates, and the sulfuric acid hydrates come into being as a consequence of dehydration of the nitric acid hydrates.

In cases of equimolecular relations between the sulfuric acid monohydrates and the water, complete dehydration of the nitric acid occurs in the mixture, and the latter is in the state of free monohydrate, despite the presence of water in the mixture. This coincides with the maximum vapor pressure of HNO_3 . Thereafter, addition of the sulfuric acid monohydrate results in reduction in the vapor pressure of nitric acid. A.V.Sapozhnikov explains this fact ~~in~~ as follows: ~~that~~ when the amount of water in the mixture becomes inadequate for formation of the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, the unhydrated sulfuric acid cleaves water away from the nitric acid, converting it into the anhydride N_2O_5 , thus reducing the strength of the HNO_3 , and consequently its vapor pressure. Thus, according to the views of A.V.Sapozhnikov, the nitric acid vapor pressure over mixed acid is governed by condition of the nitric

acid in this mixture.

Assuming the existence of a relationship between the degree of dehydration of HNO_3 in the ternary mixture $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$ (characterized by the partial pressure of the nitric acid) and the nitrating capacity of this mixture, A.V.Sapozhnikov compared the data he had ~~had~~ gathered on the nitrating capacity and the vapor pressure of the nitric acid in the corresponding ternary mixtures. In so doing, he discovered a coincidence between the maximum of ~~the~~ nitrating activity of the mixtures with respect to cellulose, and the vapor pressure of nitric acid. Moreover, basing himself upon the experiments of Vieille, who showed that 78% nitric acid, corresponding to a composition of ~~EX~~ $\text{HNO}_3 \cdot \text{H}_2\text{O}$, does not nitrate cellulose, A.V.Sapozhnikov suggested a theory of nitration mixtures in accordance with which ~~XXXX~~ it is only the unhydrated nitric acid that has the capacity to nitrate. As a consequence, the degree of nitration of cellulose is directly related to the condition of the HNO_3 mixture. When the mixture is $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, all the nitric acid is present as the monohydrate, and the acid mixture has maximum ~~XXXX~~ nitrating capacity. When the amount of water in the acid mixture is increased, nitric acid hydrates, $\text{HNO}_3 \cdot \text{H}_2\text{O}$, come into being therein. This reduces the reactivity of the nitric acid.

The nitrating ability of mixed acid diminishes also if the amount of water is inadequate to take up the entire sulfuric acid as hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, in which case the unhydrated sulfuric acid cleaves water away from the nitric acid converting it to N_2O_5 .

Sapozhnikov was in error in assuming that nitric anhydride yields a lower vapor pressure than nitric acid, and does not cause nitration.

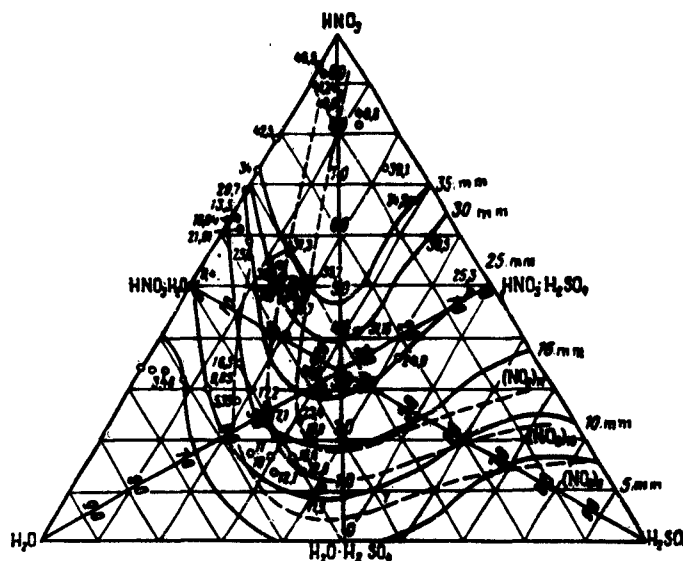


Fig.1 - A.V.Sapozhnikov's Diagram

A.V.Sapozhnikov depicted the data of his experiments with respect to vapor pressure and the nitrating activity of mixtures on a Gibbs' phase rule plot (Fig.1). The vertices of the triangle correspond to 100% composition of each of the components of the mixture H_2SO_4 , HNO_3 , and H_2O . The sides of the triangle correspond to the respective binary mixtures. Each point within the triangle represents the composition of a ternary mixture. The compositions of the mixtures are given in molecular percent. The solid curves on the diagram correspond to mixtures having identical nitric acid vapor pressure. The broken lines represent mixtures having identical nitrating capacity for cellulose.

34 Graphic comparison illustrates the presence of a specific relationship between the direction of the curves bounding the regions of the cells having an identical degree of nitration, and the direction of curves equal to the partial pressure of

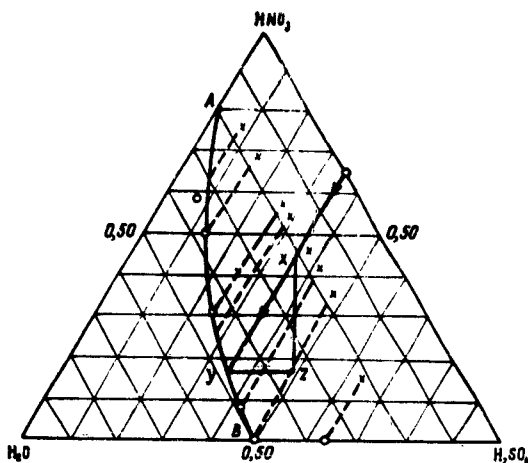


Fig.2 - Change in Strength of Nitro Mixture in the Nitration of Mononitrobenzene

the nitric acid vapor in ternary mixtures.

A.G.Gorst (Bibl.127) showed that A.V.Sapozhnikov's theory of nitration is also applicable to the case in which aromatic hydrocarbons are nitrated if the acid mixture is characterized not by its ~~initial~~ initial but final composition. This necessity arises from the fact that the composition of the acid mixture changes substantially in the process of nitration of aromatic hydrocarbons. The change in composition is due to the low module (module is the ratio of the weight of the mixed acid to the weight of the substance undergoing nitration). In the ~~nitration~~ nitration of cellulose, the module is high, and therefore the composition of the acid mixture during the entire period of nitration remains virtually unchanged. Change in the strength of the nitro mixture in the process of nitration may be illustrated graphically on a diagram (Fig.2), in which the compositions are expressed in molecular percent.

In the process of nitration, the molar percent of sulfuric acid in the nitro mixture remains unchanged. Therefore a mixture whose initial composition is x will react with the compound undergoing nitration until its composition, varying along the straight line ~~xy~~ xy achieves a limiting value y , at which the reaction ceases for all practical purposes. This same point of cessation of reaction y will be achieved with any other nitro mixture, the initial composition of which lies between x and y . The yield of nitro products when acid of composition x in moles per mole of nitro mixture is expressed by the straight line xz , as this straight line measures the consumption of nitric acid.

The ~~curve~~ ^{curve} AB is the curve for acid mixtures of the limiting composition. The acid mixture of limiting composition is that in which the nitration reaction virtually ceases. This curve is analogous to the curve obtained by ~~A.V.Sapozhnikov~~ A.V.Sapozhnikov for cellulose nitrates.

A similar investigation was conducted in 1940 by Lewis and Suen (Bibl.128). They determined the partial pressure of nitric acid and water vapors over mixed acid, and also studied the reaction rate of nitration of nitrobenzene by acid mixtures of various compositions. The results of measurements of vapor pressure, applied to a phase rule plot, or compared to the curves for constant velocities of nitration (isobells). The authors emphasize the remarkable parallelism between nitration velocity and vapor pressure above the reaction mixture. Assuming that in the ternary mixture $H_2SO_4-H_2O-HNO_3$ only HNO_3 and H_2O are at all significantly volatile, the authors ~~hold~~ hold that the nitration velocity is a function of the ratio $\frac{P_{HNO_3}}{P_{H_2O}}$.

A shortcoming of A.V.Sapozhnikov's theory is the erroneous concept to the effect

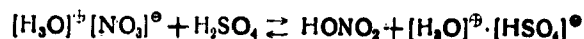
that nitric anhydride is formed in the process of dehydration of nitric acid by sulfuric acid, and the assertion that N_2O_5 is incapable of nitrating cellulose.

35

The concept of the structure of nitric acid and its mixtures with sulfuric acid presented by Hantsch on the basis of studies of cryoscopy, electrical conductivity, and spectrum analysis, made it ~~possible~~ possible for Farmer (Bibl.129) to carry further the theory of A.V.Sapozhnikov.

According to Hantsch (Bibl.97), nitric acid plays the role of a base in mixtures of nitric and sulfuric acids, and sulfuric ~~acid~~ acid acts as the acid.

Aqueous nitric acid has the structure of a salt $[H_3O]^+[NO_2]^-$. When sulfuric acid is added thereto, the latter removes water from the hydroxonium salt of nitric acid:



and thereby increases the content of pseudo nitric acid ($HONO_2$). The addition of a specific amount of sulfuric acid to the nitric acid makes it possible to convert it completely to the pseudo state. Further increase in ~~the~~ the amount of sulfuric acid and reduction in the water content of the mixture results in formation of nitrocidium sulfate $[H_2NO_3]^+[SO_4H]^-$ and, correspondingly, to a reduction in the amount of pseudo nitric acid.

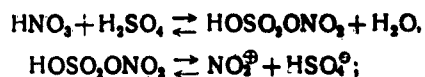
In Farmer's opinion (Bibl.129), it is specifically the pseudo nitric acid that participates in the nitration of aromatic hydrocarbons and the etherification of alcohols and cellulose.

Other investigators ~~(Bibl.130, 131)~~ (Bibl.130, 131) have advanced analogous views with respect to the mechanism of nitration by mixed acid.

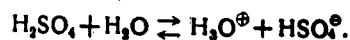
The large number of studies devoted to investigation of mixed acid and of the

nitration reaction published in the postwar years, in which ~~the~~ pride of place must be given to those of A.I. Titov, Bennett, and Ingold, indicate that nitronium cations, dissociation products of nitric acid, are present in mixed acid ~~in~~ as well as in strong nitric acid.

The appearance of the nitronium cation from ~~the~~ nitric acid in the presence of sulfuric acid may be explained by the dissociation of nitro sulfuric acid:



water reacts with H_2SO_4 to form hydroxonium ions $\text{H}_3\text{O}^{\oplus}$ and the bisulfate HSO_4^{\ominus} :



Therefore, the reaction between nitric and sulfuric acid may be expressed in terms of the equation



The numerous studies representing investigations of the structure of the acids have finally confirmed the validity of this equation, in accordance with which sulfuric acid converts nitric acid into the NO_2^{\oplus} cation (Bibl. 98, 132, 133).

Determination of the reduction of the freezing point of 100% sulfuric and pyrosulfuric acids, upon addition of nitric acid, has shown that this is actually accompanied by the formation of four particles for each molecule of nitric acid, as the equation presented demands (Bibl. 134, 135).

The high electrical conductivity of mixed acids, discovered by A.V. Sapozhnikov (Bibl. 125), and studied in detail by other investigators confirms the formation of ions when nitric acid is dissolved into sulfuric.

XX Upon electrolysis of HNO_3 in oleum solution, it was found that nitric acid moves toward the cathode, and consequently nitric acid in this solution is in the form of a cation (Bibl.136).

The absence of free nitric acid in the nitrating mixture, when it contains less than 10% water, and in an anhydrous mixture is confirmed by A.V.Sapozhnikov's discovery of the exceedingly low vapor pressure of nitric acid over such a mixture (Bibl.125, 137).

36 In investigations of the Raman spectra of solutions of nitric acid in sulfuric acid, a 1400 cm^{-1} line was found, the intensity of which diminished with increase in the water content of the mixture (Bibl.138). On the basis of analogy with lines yielded by biatomic and linear triatomic particles, it is held that the line of that frequency/represents the nitronium cation $\text{O}=\text{N}=\text{O}^{\oplus}$ (Bibl.137, 139).

The Raman spectrum method has now been employed to develop a procedure for quantitative determination of the nitronium ion in nitric acid and mixed acid (Bibl.140). It was found that the Raman spectrum line corresponding to the NO_2^{\oplus} ion disappears completely in nitric acid when a water content of 5 - 6% is attained, but at a considerably higher water content in mixtures with sulfuric acid.

Inasmuch as, in ternary $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ mixtures, the water is taken up primarily by sulfuric acid, it will follow that the presence of the nitronium cation may be noted at higher water contents (Bibl.132, 141). Reduction in the NO_2^{\oplus} content with addition of water to mixed acid is explained by the formation, under these conditions, of the hydroxonium and bisulfate ions:



which shift the equilibrium of the nitronium cation formation reaction to the left.

From measurement of the brightness of lines at 1400 cm^{-1} in the Raman spectrum of this light, the equilibrium constant of the reaction referred to above is found to equal approximately 30 - 42. From kinetic data, the value of this constant would be 31 - 36. Consequently, if a sufficiently ~~EX~~ large excess of sulfuric acid is present, and if the water content is small, nitric acid undergoes virtually complete transformation into the nitronium cation (for example, in an 0.2-molar solution of nitric acid in 98 - 100% sulfuric acid). However, in an 87% sulfuric acid solution of the same amount of nitric acid, only 12.7% of the ~~NITRONIUM~~ nitric acid goes into nitronium cations (Bibl.132, 142).

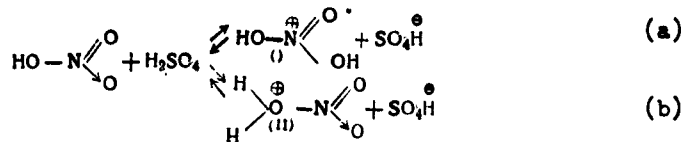
In anhydrous mixed acid, increase in the nitric acid content is accompanied by a reduction in the degree of conversion thereof into nitronium cation, as is evident from the data in Table 4 due to Chedin (Bibl.138) on the basis of the brightness of the 1400 cm^{-1} line in the ~~RAMA~~ Raman spectrum.

Table 4

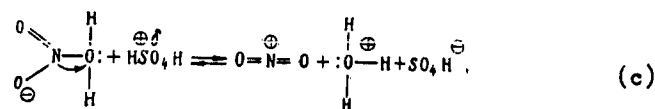
a)	H ₂ SO ₄	95	90	85	80	60	40	20	10	0
	HNO ₃	5	10	15	20	40	60	80	90	100
b)		100	100	80	62,5	28,8	16,7	9,8	5,9	1

a) Composition of mixed acid, in %; b) Amount of HNO₃, converted to NO₂⁺, in %

According to A.I. Titov (Bibl. 98), the formation of nitronium cation in mixed acid begins with the attachment of a proton to a ~~the~~ nitric acid molecule in two possible directions:

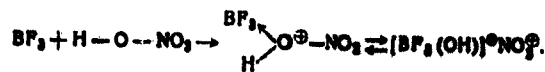


In accordance with eq.(a), it is the Hantsch ~~nitronium~~ ^{nitracidium} cation (I) that is formed, whereas in accordance with eq.(b), it is the ~~nitronium~~ ^{nitroxonium cation} (II). The latter goes into an equilibrium reaction with the second molecule of the sulfuric acid:



which results in the formation of free nitronium cation. As a consequence of the acid-base nature of the reaction (a, b, c), the formation of nitronium cation in strong acids grows very rapidly, in proportion to the acid function of the reactant, whereas in the ordinary nitrating mixture or in strong nitric acid, it occurs almost instantaneously.

37 Formation of nitronium cation with other strong acids, for example, with boron fluoride, ~~XI~~ follows analogous equation

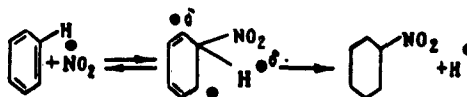


reaction are determined as a consequence of the competition between these two equilibria, inasmuch as, on the one hand, an increase in the strength of the sulfuric acid increases the number of NO_2^{\oplus} ions, whereas on the other hand it reduces the quantity of the most active proton acceptor: the HSO_4^{\ominus} ion.

Thus, according to Bennett, the nitration reaction is the result of an encounter among ~~XXX~~ ^{three} particles: molecules of the aromatic compound, the nitronium ion ~~XXX~~ NO_2^{\oplus} , and the proton acceptor which may ^{be} HSO_4^{\ominus} . The velocity of this reaction depends upon the equilibrium between the first two reactions proceeding in the mixed acid. A change in the velocity may be induced not only by reduction in the NO_2^{\oplus} contents but by a change ^{the} in/proton acceptor; for example, in an anhydrous mixture, H_2SO_4 will be the proton acceptor. Under these conditions, the effect of the nature of the compound undergoing nitration upon the nitration speed is left out of consideration.

Views analogous to those of Bennett, have been put forth by other investigators (Bibl. 145, 146). However, as shall be indicated below, studies of the nitration rate, employing isotopes, have refuted this pattern.

The course of nitration of aromatic compounds by the nitronium cation is expressed by A.I. Titov (Bibl. 83, 98, 147) as an ion-complex reaction:

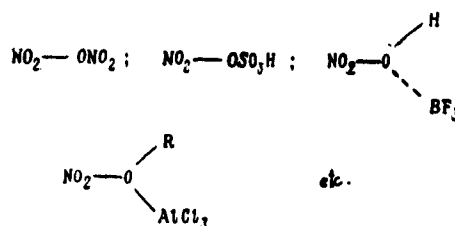


When the NO_2^{\oplus} reacts with the ring, a critical complex is formed, partly as a result of the energy of activation. Hydrogen then splits off in the form of an ion

of the solvent of high polarity, and the complex converts ~~the~~ to a nitro compound.

The energy required for activation of formation of the nitro compound must be the smaller, the deeper the reaction between NO_2^{\oplus} and ArH can go as a consequence of complex formation as such.

A.I. Titov believes it possible that the capacity to nitrate may be manifested by such highly ~~electrophilic~~ electrophilic compounds as



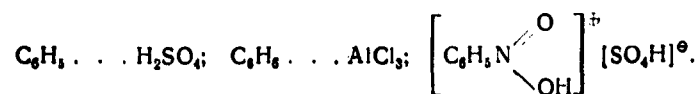
in view of the fact that the condition of the NO_2 group therein is similar to that for the nitronium cation. Consequently, the activating effect of such additions to nitric acid ~~as~~ as H_2SO_4 , AlCl_3 , BF_3 , etc., is explained by an increase in the electrophilic ~~electrophilic~~ nature of, and the fact that the nitrogen atom of the nitrating agents of the structure indicated above are not saturated in terms of coordination.

In the extreme case, a nitronium cation NO_2^{\oplus} , of maximum activity appears. However, in the pure condition, ~~when~~ when solvation has not occurred, NO_2^{\oplus} may exist only in the gas ~~phase~~ phase, according to A.I. Titov. However, the activity of NO_2^{\oplus} in solvents in which it is formed depends upon the degree and nature of its solvation (Bibl.98).

For example, A.I. Titov explains the diminished activity of a mixture of nitrogen and hydrogen fluoride by the deep solvation of NO_2^{\oplus} by hydrogen fluoride and the

fluoride ion, due to the small size of the fluorine atom. .

According to A.I. Titov (Bibl. 98), sulfuric acid, and other nitration activators, ⁱⁿ also play a negative role/that they are capable of reacting with aromatic compounds to yield complexes, salts, and ~~MI~~ cations, for example



Compounds of this type undergo nitration considerably more slowly than do the initial compounds, as a consequence of the sharp reduction of electron density therein.

It is from this aspect that A.I. Titov examines the causes for reduction in nitration velocity of many compounds by mixed acid ~~XXXX~~ when the strength of the sulfuric acid is increased above a particular value. The reaction rate of nitration is determined by the nature of the compound being nitrated, which is capable of reacting ^{NAT} only with nitric but with sulfuric acid. The reaction with sulfuric acid in the presence of nitric acid occurs only when there is an excess of the former.

Later, analogous views were set forth by Gillespie (Bibl. 148), Ingold and Samuelsen (Bibl. 99).

A.I. Titov's theory provides a ready explanation for the nitration of many aromatic compounds (benzene, toluene, mononitrotoluene, etc.) ~~XXXX~~ both by nitric acid alone, and by mixed acid. In mixed acids containing more than 10% water, the quantity of NO_2^+ cation will be small, but in view of the acid-basic nature of the reaction by which it is formed, and the highly nucleophilic nature of aromatic

compounds of the type of toluene, the loss of NO_2^{\oplus} cation due to consumption in the process of nitration should be made good very rapidly (Bibl.143, 149).

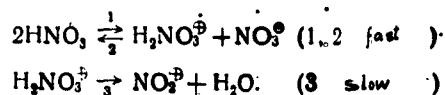
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Studies made in the last few years have provided final confirmation of the nitration reaction ~~XX~~ mechanism suggested by A.I.Titov. Thus, Melander (Bibl.150), having studied the effect of the rate of cleavage of the proton, ~~deuterium,~~ ^{deuterium,} and tritium ~~upon~~ upon the nitration rate of toluene, benzene, naphthalene, etc., has shown that the rate of cleavage of hydrogen of various atomic weights does not affect the nitration reaction velocity. Identical velocities ~~XX~~ were found by other authors on the nitration of nitrobenzene and pentadeuteron nitrobenzene (Bibl.151), as well as of benzene and monodeuter^ebenzene (Bibl.152) in a sulfuric acid medium.

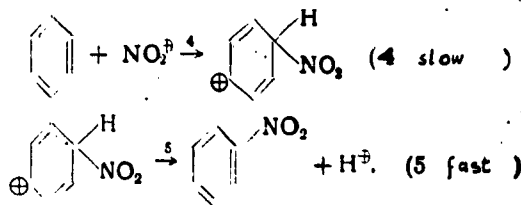
On the basis of theoretical considerations, the stage in which the disruption of the bond between the hydrogen atom and the aromatic ring occurs, in the case of tritium, ~~proceeds~~ ^{proceeds} only about 20 - 30 as fast as in the case of protium (Bibl.153). Therefore, the absence of differences in the nitration rates testifies to the fact that this reaction occurs in two stages, the slower of which (that which determines its velocity) is the stage in which the bond between the carbon atom and the hydrogen atom replacing it is not broken.

Bennett (Bibl.154), ⁱⁿ discussing the question of the effect of sulfuric acid upon the nitration rate of an aromatic compound, abandoned his theory previously advanced (Bibl.144). He points out that the rate of nitration depends upon the solubility in sulfuric acid of the compound being nitrated and upon the degree to which nitric acid is converted into the NO_2^{\oplus} cation under the influence of a large excess of sulfuric acid.

Ingold and his associates, abandoning their former views with respect to the chain mechanism of the nitration reaction (Bibl.114, 155) advanced a two-stage mechanism for the reaction, in which, like A.I.Titov, the proton loss does not affect the reaction velocity. According to ~~XX~~ Ingold (Bibl.99, 108, 109), the formation of the NO_2^{\oplus} cation proceeds via the following stages:



As this occurs, strong acids such as sulfuric acid may also serve as hydrogen donors in the formation of $\text{H}_2\text{NO}_3^{\oplus}$. The nitro compounds are formed in two stages:



~~XX~~ This mechanism assumes that after the nitronium cation has joined with the aromatic atom of carbon, ~~XX~~ ^aproton ~~XX~~ attached to this atom cleaves off almost instantaneously. Thus, this mechanism rules out the trimolecular reaction assumed by Bennett.

Proceeding from consideration of the effect of sulfuric acid as a highly polar solvent, ~~IX~~ Ingold holds that the reaction rate of nitration in anhydrous sulfuric acid has to be from 2 - 4 times faster, but the situation is complicated by the fact that the compound being nitrated forms salt-like complexes with sulfuric acid. They are incapable of reaction, and, upon the addition of water, they undergo partial

dissociation which, under these circumstances, facilitates nitration (Bibl.99, 156).

Williams
However, ~~Williams~~ and associates (Bibl.157), criticising Ingold's theory, hold that reduction in the nitration velocity, occurring when one changes from 90% to 100% H_2SO_4 , is no longer explicable in quantitative terms.

From the foregoing it is clear that Ingold's latest theory is highly similar to that of Titov.

40 Section 4. Kinetics of Nitration by Mixed Acid

a) Nitration under Homogeneous Conditions

The kinetics of the nitration reaction of aromatic compounds by mixed acid has had rather adequate investigation. One of the first studies was one of Martinsen (Bibl.158) who studied the relationship of the nitration velocity of a number of aromatic ~~aromatic~~ compounds to the strength of sulfuric acid used as the medium. The sulfuric acid was taken in considerable excess with respect to the nitric acid and the compound undergoing nitration. Therefore, the reaction occurred under homogeneous conditions, and the strength of the sulfuric acid underwent practically no change. The nitration velocity constants were computed by Martinsen on the equation for bimolecular reactions, and, having found them to be in good agreement for various time intervals, he demonstrated that the nitration reaction is a second-order reaction. Data on experiments with nitration of nitrobenzene in
of
sulfuric acid ~~of~~ various strengths are presented in Table 5.

When these results are presented in diagrammatic form (Fig.3) one readily sees a maximum in the curve of nitration velocity constants, corresponding to a content of 0.63 molecule of water per molecule of sulfuric acid (representing 89.5% H_2SO_4).

Table 5

a)	K_0	K_{25}	$\frac{K_{25}}{K_0}$
0,01SO ₃	0,036	0,22	6,1
0,30H ₂ O	0,085	1,50	17,6
0,63H ₂ O	0,280	3,22	11,5
1,03H ₂ O	0,017	0,18	10,6

a) H₂O or SO₃ Content per 1 mole H₂SO₄

A.V. Sapozhnikov

Thus, Martinsen, like ~~XXXXXXXXXX~~ demonstrated that the positive effect of

sulfuric acid upon nitration velocity occurs only up to a specific strength limit.

When this limit is passed, the sulfuric acid ceases to play the role of a reaction

promoter, and a sharp drop in the curve of the nitration velocity constants testifies

to the negative effect of sulfuric acid of high strength.

~~XXXXXXXXXXXXXXXXXXXX~~

Subsequently, it was found by the work of

other investigators (Bibl. 131, 144, 159, 160) that

the nitration velocity constant of the majority of

aromatic compounds ~~XXXXXXXXXX~~ diminishes by a factor of

3 - 4 when the strength of the sulfuric acid is

increased from 90 - 100% having first passed through

a maximum obtained at various strengths, 89.5% in

the case of nitrobenzene, and 93% in the case of

dinitrotoluene). For compounds such as benzoic

acid and benzene sulfonic acid, the reduction is by a factor of 18.5 and 11.5,

respectively.

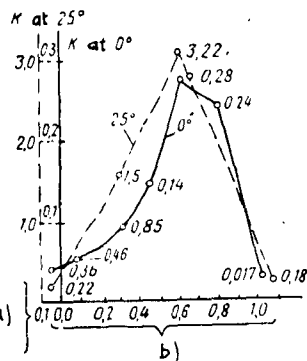


Fig. 3 - Martinsen's Curves

~~XXXXXXXXXXXXXXXXXXXX~~

a) Mole SO₃ per mole H₂SO₄;

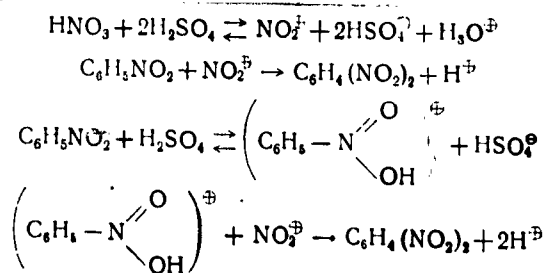
b) Mole H₂O per mole H₂SO₄

The maximum in the constant of nitration velocity by mixed acids is explained

by Bennett and associates (1933) on the fact that different particles act as proton acceptors in sulfuric acid of different strengths: HSO_4^- being the acceptor in dilute acid, H_2SO_4 in anhydrous acid, and HS_2O_7^- in acid containing free sulfuric anhydride. However, as has already been shown, the speed of the nitration reaction is determined only by the rapidity with which the critical complexes ^{led} formed, and is not dependent upon the speed with which the proton leaves and, consequently, cannot be determined by the nature of proton acceptor (Bibl.98, 156).

The ~~XXX~~ existence of a maximum in the nitration reaction speed at a given sulfuric acid strength may be explained on the basis of the theory of A.I. Titov (Bibl.98, 147), in accordance with which the activating additives play a dual role. On the one hand, they convert nitric acid into its active nitrating form, while on the other they play a negative role in that they are capable of reacting with aromatic compounds to yield complexes. The entry of aromatic compounds into a complex acts upon their reactivity in a manner similar to the ~~XXX~~ introduction of meta-orienting substituting groups into the ring: nitro groups, sulfó groups, etc. It is from this point of view that Titov examines the cause of reduction in the nitration speed of many compounds by mixed acid when the strength of the sulfuric acid is raised above a particular level. Samuelson's data completely confirm this new point (Bibl.99).

The equation for the nitration reaction of, for example, nitrobenzene, as conceived by A.I. Titov, may be written in the following form:



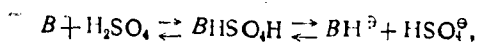
Then, the expression for the reaction speed will appear as follows

$$\frac{d[\text{C}_6\text{H}_4(\text{NO}_2)_2]}{dt} = K_1 [\text{NO}_2^+] [\text{C}_6\text{H}_5\text{NO}_2] + K_2 [\text{NO}_2^+] \left[\left(\text{C}_6\text{H}_5 - \text{N} \begin{array}{l} \text{O} \\ \text{OH} \end{array} \right)^+ \right]$$

Here, it is only the first term, expressing the rate of reaction with free nitrobenzene that has real significance, as the velocity of nitration of the cation of the nitrobenzene complex is exceedingly low.

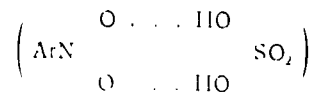
An increase in the strength of the sulfuric acid, which raises the content of nitrating agent (the nitronium cation), at the same time continually converts the free nitrobenzene into the inactive condition of the cation. The dual and mutually opposing effects of the sulfuric acid upon the nitration speed is what is responsible for the appearance of a maximum. This explanation is confirmed by the fact that the maximum disappears when the content of the compound being nitrated is increased. In this situation, the relative loss of the compound being nitrated, caused by its conversion into a complex, will be diminished.

Gillespie (Bibl.161), studying the basicity of nitro compounds by determining the freezing points of their solutions in sulfuric acid, with trinitrotoluene and other substances, demonstrated the possibility of substantial ionization in accordance with the following mechanism



in which B is an aromatic nitro or sulfo compound. He determined that a 0.1-molar solution of trinitrotoluene undergoes only 9% ionization in anhydrous H_2SO_4 .

~~XXXX~~ while nitrobenzene is 41% ionized, and para-nitrotoluene is 70% ionized, approximately ~~XXXX~~ (in 75% H₂SO₄). Brand and associates (Eibl.137), having determined the ionization constants of aromatic nitro compounds in 99% sulfuric acid, obtained analogous results for TNT, para-nitrotoluene, and nitrobenzene. It is assumed (Eibl.162) that the distinctive features of the absorption spectra of solutions of aromatic nitro compounds in sulfuric acid may be explained by the presence of compounds of the type ArNO₂ · H₂SO₄



Compounds of this type must ~~XXXX~~ necessarily undergo slower nitration.

Gillespie (Eibl.143) regards the solution of organic compounds in sulfuric acid as the initial chemical process, and that it ~~XXXXXXXX~~ proceeds in accordance with the equation indicated above. Spectroscopic data (Eibl.162, 163) make it possible to conclude that the complex formation of nitro compounds ends when the strength of the H₂SO₄ is 90 - 98%. Reduction in the formation of the ArH · H₂SO₄ complex or of its cation ArH⁺ in the nitrating mixture is ~~XXXXXXXX~~ achievable by addition of potassium bisulfate (HSO₄⁻) and other bases, including excess nitric acid (Eibl.145) and nitro compounds (Eibl.137).

However, the ~~XXXXXXXX~~ ^{existence} of a maximum of nitration velocity is also found in compounds not subject to complex formation even with 100% sulfuric acid. Therefore,

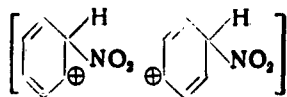
N.N.Vorozhtsov (Bibl.164) holds that the reduction in the reaction rate upon changeover ~~XXXXXXXX~~ from 92% sulfuric acid to a stronger acid may also be due to the change in the nature of the reaction medium [the change in the reaction rate is sometimes measurable by a factor of hundreds when the solvent is changed, as was noted by N.A.Men'shutkin (Bibl.165)] a long time ago. 90% sulfuric acid is ionized to a considerable degree, but anhydrous is ionized little, and it is quite probable that this change in the nature of the solvent must necessarily result in a reduction in reaction velocity.

It has been ~~XXX~~ observed that compounds that are not subject to the addition of a proton have minimum nitration speed in 100% sulfuric acid. This speed increases upon addition of ~~XXXX~~ either water or sulfuric anhydride to the monohydrate. At the same time, the rate of reaction in fuming sulfuric acid is lower than in 100% sulfuric acid in the case of substances ~~XXXX~~ capable of proton addition. N.N.Vorozhtsov (Bibl.164) sees the reason for this in the greater acid function of fuming sulfuric acid and in the higher degree of ionization of organic substance conditioned by this fact.

In ~~XX~~ introducing corrections into the degree of ionization, and in computing the reaction velocity constants, with consideration for the strength only of the existence of a unionized substance, the minimum velocity constant in 100% H_2SO_4 is also observed in ~~XX~~ other substances.

The probable explanation for the minimum reaction velocity in 100% sulfuric acid lies in the fact that the dielectric constant ~~XXXXXXXXXXXXXXXXXXXX~~ of 100% H_2SO_4 is greater than that of the dilute acid and of fuming sulfuric acid (which are more highly ionized

than is the monohydrate). Inasmuch as upon nitration, the formation of the transient complex



43 is related to the distribution of the charge formerly characteristic of the nitronium ion to the aromatic ring, it follows that, in accordance with the general theory of the effect of the solvent, the velocity of this type of reaction ~~is~~ has to increase with ^{an}reduction in the dielectric constant of the solvent (Bibl.148).

A.I. Titov (Bibl.98) ^{also} explains ~~instances~~ ^{instances} of this type by the effect of the composition upon the dielectric constants, the solvating properties of the medium, and other factors, while simultaneously holding it to be possible that complexes of the aromatic compounds may be formed with ~~electron~~ ^{electron} donor particles, such as H_2O , NO_3^{\ominus} , as well as the possibility of conversion thereof into anions. Conversion of aromatic compounds into such states increases their activity when subjected to nitrating agents.

A.I. Titov explains the very pronounced increase in nitration speed when water is added to a solution of ~~the~~ aromatic acids in an anhydrous mixed acid by the coincidence of the above processes. Substitution of a medium of low polarity (CCl_4) by one having a high dissociative capacity (CH_3NO_2 , H_2O) greatly accelerates the reaction with the nitro phenols. A.I. Titov sees the cause of this in the increase in the degree of conversion of nitro phenols into electron donor anions (Bibl.103).

b) Nitration under Heterogeneous Conditions (Bibl.128)

Under industrial conditions, the process of nitration normally occurs under heterogeneous conditions, i.e., when the two layers are present - an organic and an acid layer. The principles of ~~the~~ homogeneous nitration, examined above, cannot be applied in all respects to heterogeneous nitration. The reason for this is the fact that the speed of heterogeneous nitration is naturally less than that of homogeneous, and depends upon a larger number of factors.

The speed of homogeneous nitration depends, as we know, not only upon the nature of the compound being nitrated, but upon the temperature and the composition of the nitrating mixture, which is a function of two independent variables, inasmuch as the mixture consists of the following components: sulfuric acid, nitric acid, and water. Under conditions of heterogeneous nitration, it also depends upon the composition of the organic ~~of~~ phase, the relative ~~of~~ volume of the two liquid phases, and upon the method and degree of mixing. Under heterogeneous conditions, it is necessary to make clear the volume of each phase and the phase interface.

The complexity of the problem of studying reaction velocity in a system having two phases lies in the fact that the reacting components may be distributed among both phases, and the rate of reaction in each phase will be determined by the ^{these} concentration of/components therein. The reaction may also proceed at the phase interface.

Under heterogeneous conditions, the reaction begins and proceeds, to some degree, where the substances of the different phases first meet, i.e., at the

interface. The reacting substances have to approach this interface, and the reaction products must be able to leave it. Consequently, in the general case, the phenomenon of diffusion, and methods for accelerating it are of considerable importance for the course of the reaction in a heterogeneous medium. The rate of conversion therefore depends ~~upon the~~ ^{upon the} rate at which the reacting substances are transferred from the different phases ~~and~~ to the reaction zone, upon the velocity of the chemical reaction, and upon the speed with which the reaction products are removed from the reaction zone. Moreover, the speed of the total process of conversion is determined by the speed of the slowest process involved, and the overall regularity is governed to a greater or lesser degree by the relationship between the velocities of the processes constituting the whole.

In the case of slow reactions, the process does not succeed in occurring at the interface, and the reaction zone expands to include the entire volume of the phase into which the reacting components penetrate. Where reactions of this type are concerned, the area of the interface has a less significant effect upon the degree of conversion than does the volume of the phase in which the reaction occurs. In this situation, agitation serves only to saturate one phase with the other.

Readily nitratable substances react at the interface, and the speed of this reaction is significantly affected by the size of the surface, which is, in turn, frequently governed by the intensity of stirring.

Substances that nitrate with difficulty react chiefly in the acid layer, whereas in the organic layer the reaction velocity is quite low (for example, in the

case of nitrobenzene, the nitration velocity and the organic layer is only one tenth as great as that in the mineral layer (Bibl.128)]. The lower reaction speed in ^{the} organic layer is explained by the fact that it is chiefly nitric acid that goes into this layer. As we know, in the absence of sulfuric acid, this substance has a lower ~~XXXX~~ nitrating capacity than otherwise.

speed
The reaction/under heterogeneous

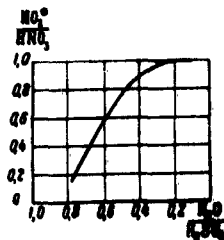


Fig.4 - Dependence of Ratio of NO₂⁺/HNO₃ Concentration to Strength of Sulfuric Acid, Expressed as H₂O/H₂SO₄ Ratio

conditions depends upon the composition of the acid mixture in each layer. The temperature dependence of the speed of the nitration reaction under heterogeneous conditions is somewhat lower than under homogeneous conditions. Thus, when temperature is increased by 10°, the reaction speed rises by less than 100%. This latter fact is explained by the fact that, under the

given conditions, the velocity of the process is determined by the rate of diffusion. When two layers are present (as is normally the case IX under industrial conditions in nitration), one does not see a maximum velocity at any particular strength of sulfuric acid. The reaction speed (at a constant nitric acid strength) is approximately directly proportional to the ratio

$$\frac{[H_2SO_4] - [H_2O]}{[H_2SO_4]}$$

On the one hand, this ratio determines the solvent ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX~~ capacity of the acid and, consequently, the concentration of the ~~XXXX~~ compound being nitrated in the mineral

phase and, on the other hand, it governs the concentration of NO_2^{\oplus} , inasmuch as it depends upon the strength of the free H_2SO_4 (not bound in the form ~~III~~ of H_3C_+ and HSO_4^{\ominus}).

The fact that there is no velocity maximum on nitration in a heterogeneous medium is explained, according to A.I. Titov, by the fact that the ~~concentration~~ concentration of the substance being nitrated is constant and by the relatively smaller losses thereof, as a consequence of attachment to the sulfuric acid in an inactive complex, and also by the increase in the solubility of the substance being nitrated in the acid layer, where the reaction chiefly proceeds when sulfuric acid strength is increased. Moreover, in a ~~heterogeneous~~ heterogeneous process, relatively more HNO_3 is ~~usually~~ usually employed for nitration than in a homogeneous. However, increase in the nitric acid content in strong sulfuric acid leads to increasing the content of the NO_2^{\oplus} ions, as is evident from the curve in Fig. 4.

C.
EX) Effect of Substitute Groups upon Velocity and Result of Nitration

The nature of the substance being nitrated has a major influence upon the nitration reaction velocity, and also upon the composition of the isomers of the nitro compounds resulting. In the case of aromatic compounds, this effect is determined primarily by the substitute in the benzene ring. A large number of experiments have established the fact that the new substituting ~~group~~ group enters the aromatic ring in a position determined primarily by the nature of the substituting groups already present in the ring, and is governed only to a very small degree ~~III~~ by the properties of the new substituting group. It has been found that substituting groups present in benzene guide the newly entering

45

~~XXXXXXXX~~

substituting group into specific positions with respect to themselves.

Gollesman divided all substituting groups into two series and arranged them with ~~XXXX~~ each of the series in terms of the relative capacity to govern position. The substituting groups guiding the new substituting group into the ortho or para position are called groups of the first order, and those guiding into the meta position are called second-order groups. Substitution in compounds containing first-order substituting groups usually goes more readily than in the initial ~~XX~~ (unsubstituted) ~~XXXXXXXXXX~~ compound. Contrariwise, substitution in groups containing the meta-oriented group proceeds with greater difficulty than in the initial compounds, requiring higher temperature, higher reactance strength, etc. At present, orientation is held to be related to the polarity of the substituting group and that of the reactant.

Substituting groups of the first type, which are electron donors, increase the electron density of the ~~XXXX~~ ^{para-} and ortho-carbon atoms, and considerably increase their reactivity. The second type of substituting groups, which are electron acceptors, pull electrons away from other carbon atoms in the benzene ring, and this occurs primarily from ~~XXXX~~ ^{ortho-} and para-carbon atoms, with substitution proving possible only in the meta position.

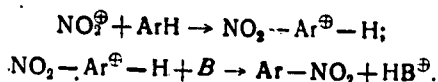
The usual substitution reactions are induced by reactance of the electrophyl^{ic} type. From this it follows that if the ring has a substituting group that repels electrons - an electron donor - it will activate^{ate} the benzene ring, communicating a negative charge to the carbon atoms. Contrariwise, a substituting group that attracts electrons and communicates a positive charge

deactivate the ring with respect to the electrophilic reactance, and consequently with respect to the NO_2^{\oplus} cation, which is the nitrating agent.

In accordance with current views, nitration EX falls into the category of electrophilic substitution reactions, inasmuch as it incorporates an attack by the electrophilic residue NO_2^{\oplus} upon an EX aromatic ring, which may be expressed by the general equation



The electrophilic substitution reaction proceeds in two stages. In the first stage, the electrophilic reactance, which in the given case is NO_2^{\oplus} (having a nitrogen atom not saturated in terms of coordination) joins the electrophilic compound and forms a transient complex of a donor-acceptor character. In the second stage, the atom of hydrogen leaves as a proton, and the electron pair is retained by the aromatic compound



It is assumed that the liberation of the proton is immediately followed by its attachment to the base B. However, the nitration velocity is determined solely by the speed with which the critical complex is formed.

The electron density of individual carbon atoms in the aromatic ring, which is determined by the presence of substitute groups in this ring, governs both the orientation of the nitro group entering the ring, and the speed with which this process occurs. Substitute groups in the ring orient the nitro group,

affecting the direction of motion of the NO_2^{\oplus} , and the degree of stability of the transient complex formed.

46

Table 6 shows the effect of substitute groups in the benzene ring upon the position of the entering nitro group (Bibl.166, 167). It is evident from this that the amount of meta isomer increases not only upon introduction of electrically negative substitute groups, but upon extension of the side chain. The latter has a particularly sharp influence upon the relation between the ortho- and para-isomers. With increase in the hydrocarbon radical, the yield of ortho-isomer diminishes due to the increase in para-isomer yield. This phenomenon may perhaps be related to the steric effect of the alkyl group upon substitution in the ortho-position.

Table 6.

a)	b)		
	c)	d)	e)
-F	12,4	f)	87,6
-Cl	30,1	.	69,9
-Br	37,6	.	62,4
-J	41,1	.	58,7
-CH ₃	58,8	4,4	36,8
-CH ₂ Cl	40,9	4,2	54,9
-CH ₂ CH ₃	45,4	6,5	48,2
-CH(CH ₃) ₂	30,0	7,7	62,3
-C(CH ₃) ₃	15,8	11,5	72,7
-CHCl ₂	23,3	38,8	42,9
-CCl ₃	6,8	64,5	28,7
-COOC ₂ H ₅	28,3	68,4	3,3
-COOH	18,5	80,2	1,3
-NO ₂	6,4	93,2	0,25

Group in
a) R/ring ; b) Isomer content, in %; c) Ortho-; d) Meta-; e) Para-; f) Traces

The rules governing the substitution are obviously conditioned by the relationship between the velocities of substitution of the individual atoms of carbon in the benzene derivative ring. In unsubstituted benzene, all the six atoms of hydrogen are of equal importance, and when the first substitute group is introduced into the benzene, each of the hydrogen atoms must necessarily undergo substitution at the same speed as the others, i.e., six parallel reactions have to proceed at equal speeds in benzene substitution. When the second substituting group is introduced into the singly-substituted benzene derivative, three isomers are formed (ortho-, meta-, and para-) as the consequence of the five parallel reactions of aromatic attachment (in accordance with the number of hydrogen atoms being replaced) with the substitution reactant.

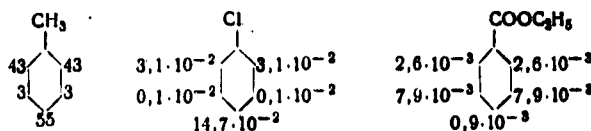
Bearing in mind the fact that there are two ortho- and two ~~meta-~~ meta-positions, of equal value, and one para-position, the consequence is that only three isomers are formed, and the relationship between the quantities of ortho- (x_o), meta- (x_m) and para- (x_p) may be represented by the following equations

$$\frac{x_o}{x_m} = \frac{K_o}{K_m}; \quad \frac{x_p}{x_m} = \frac{K_p}{2K_m}; \quad x_o : x_m : x_p = 2K_o : 2K_m : K_p$$

where K_o , K_m , and K_p are the velocity constants of the substitution reaction of the corresponding carbon atoms. If $K_o = K_m = K_p$, the relationships between the quantities of the isomers will be $x_o : x_m : x_p = 2:2:1$, i.e., 40% ortho- and meta-isomers each, and 20% para-isomer should be formed. However, in practice, the relationships between the isomers formed is entirely different. Either a single meta-isomer (with some admixture of ortho- and para-isomers) or a mixture of ortho- and para-isomer

(with an admixture of meta-isomer) is formed. This relationship indicates that there is a difference in the velocity constants of formation of the individual isomers.

Determination of the composition of the mixture of isomers obtained from the various benzene derivatives, as well as determination of the relationships between the reaction velocity constants of substitution of the benzene derivatives make it possible to compute the relative substitution speeds of the individual carbon atoms in these benzene derivatives. Thus, if we set unity as the substitution speed of one atom of hydrogen, we obtain the following substitution speeds (their values are entered at the appropriate positions in the benzene ring) in toluene, chlorobenzene, and the ethyl ester of benzoic acid:



These figures indicate an increase in the substitution speed in all the positions of the toluene ring, particularly pronounced in the ortho- and para-positions with respect to the methyl group. At the same time, in benzoic ester, substitution is retarded in all positions, and particularly in the ortho- and para-positions with respect to the etherificated carboxyl group.

When compounds ~~XXXXX~~ are nitrated with substitute groups of type two, containing oxygen (NO_2 ; SO_3H ; CHO ; COOH), with predominance meta orientation, the ratio of the ortho to the para is usually more than two to one, or else the velocity of nitration in the ortho-position is greater than in the para-position.

To clarify this ~~phenomenon~~ phenomenon, the hypothesis has been advanced that the formation of addition product in ortho-position facilitates the attraction of a positively charged nitrogen atom of the nitronium cation by a negative recharged atom of oxygen in the ring of the substitute group.

The difference between the ~~velocity~~ velocity constants of formation of the various isomers may be determined in the general case as the difference between factors independent of temperature, and as the difference in the energies of activation. It has been determined by experiments that upon substitution in the aromatic series it is a rule that the ~~difference~~ difference in the reaction velocity of formation of the individual isomers is determined only by the difference in the energies of activation. Temperature-independent factors in the velocity constants of substitution in the various positions with respect to the substituting group ~~XXX~~ are virtually identical.

For example, in the nitration of toluene, the energy of activation of substitution in the meta-position is highest, and lowest is that in the para-position with respect to the methyl group. The difference in the energies of activation and the various positions of the toluene ring is determined by the ratios:

$$E_m - E_o = 1490 \text{ cal}; E_o - E_p = 135 \text{ cal.}$$

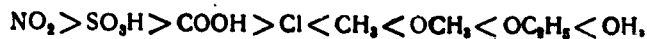
A necessary consequence of the differences in the activation energies of substitution in the various positions (with respect to the substituting group already present in the ring) is the change in the relationship of the velocity constants of formation, and consequently of the quantities of various isomers

upon change in the temperature of substitution. The isomer having the ~~lowest~~ lowest velocity of formation will be formed in the relatively greatest quantity with increase in temperature (Bibl.164).

In his studies, A.I.Tibov (Bibl.98) notes the parallelism between the influence of substitute groups upon the heat effect of the nitration reaction and upon velocity of this reaction.

Martinsen (Bibl.158) ~~studied~~ studied the influence of substitute groups on the nitration velocity constant and determined that there is a sequence of position of the substitute groups in the corresponding series. The ~~values~~ ^{values} of the nitration velocity ~~constants~~ ^{constants} of various aromatic compounds and of their nitro ~~XX~~ derivatives, due to Martinsen, are presented in Table 7.

On the basis of Martinsen's data on the nature of the effects upon the nitration reaction velocity, the substitute groups may be arranged in the following order:



wherein ~~the~~ the groups to the right of chlorine accelerate the reaction. Moreover, this acceleration is the greater, the farther to the right their location. Those to the left of chlorine inhibit the reaction.

Later investigations along these lines confirmed the validity of Martinsen's theories (Bibl.168, 169) but also revealed a number of exceptions testifying to the complex relationship existing between reaction velocity and the effects of substitute groups in orientation. Thus, only groups having a powerful effect in orienting to meta-position are entirely subject to the rule and very strongly

inhibit the reaction.

A significant influence upon the direction of the nitro group entering the ring is brought to bear by the strength of/sulfuric acid employed in nitration (Bibl.170), by the nitration catalyst (boron fluoride, Bibl.171), and also by the substitute groups in the side chain. According to Urbanski (Bibl.172), weak nitric acid (45% HNO₃) nitrates phenylnitromethane to the meta-nitro derivative, while, as we know, nitration of toluene under the same conditions yields the ortho- and para-nitro derivatives.

Table 7

Substance Being Nitrated	At K ₂₅₀	At K ₃₅₀
Nitrobenzene C ₆ H ₅ NO ₂		
Meta-dinitrobenzene C ₆ H ₄ (NO ₂) ₂	1,5	—
Benzene sulfonic acid C ₆ H ₅ SO ₃ H	0	—
Meta-nitrobenzene sulfonic acid C ₆ H ₄ (NO ₂)(SO ₃ H)	26	—
Benzoic acid C ₆ H ₅ COOH	0	—
Ortho-nitrobenzoic acid C ₆ H ₄ (NO ₂)(COOH)	100	—
Meta-nitrobenzoic acid C ₆ H ₄ (NO ₂)(COOH)	0,00005	—
Para-nitrobenzoic acid C ₆ H ₄ (NO ₂)(COOH)	0,000009	—
2,4-dinitrotoluene C ₆ H ₃ (CH ₃)(NO ₂) ₂	—	0,000043
2,4-dinitrometaxylene C ₆ H ₂ (CH ₃) ₂ (NO ₂) ₂	0,004	0,013
2,4-dinitromesitylene C ₆ H(CH ₃) ₃ (NO ₂) ₂	6,65	—
Ortho-chloronitrobenzen C ₆ H ₄ Cl(NO ₂)	7,15	—
Meta-chloronitrobenzene C ₆ H ₄ Cl(NO ₂)	0,39	1,23
Para-chloronitrobenzene C ₆ H ₄ Cl(NO ₂)	0,18	0,47
2,4-dinitroanisole C ₆ H ₃ (OCH ₃)(NO ₂) ₂	0,17	—
2,4-dinitrophenetole C ₆ H ₃ (OC ₂ H ₅)(NO ₂) ₂	0,65	—
2,4-dinitrophenol C ₆ H ₃ (OH)(NO ₂) ₂	0,85	—

The introduction of a second nitro group into the phenylnitromethane ring ~~(Bibl.173)~~ (Bibl.173) occurs only ~~EX~~ under the effect of strong mixed acid (50% HNO₃ and 50% H₂SO₄) at 65°C.

The chemical activity of the aromatic compound and the orientation upon also nitration/depend, according to studies by A.I.Titov (Bibl.98, 103) upon the form in which they enter into the reaction period. For example, for phenols,

these forms may be:



Activity in this series will rise from left to right, whereas for the cation and complex containing BF_3 , the orientation will be entirely different (Bibl.171).

The influence of substitute groups in the benzene ring indicates that the conditions of nitration of different compounds have to be different. This is reflected primarily upon the composition of the acid mixtures employed. Stronger acid mixtures have to be used as ~~stronger~~ ^{groups} tending to inhibit nitration are introduced into the compound. Thus, when toluene is nitrated to mononitrotoluene, the sulfuric acid must be of no less than 70 or 72% strength, whereas in nitration of mononitrotoluene to dinitrotoluene it must not be lower than 80 - 82%, and in nitration of dinitrotoluene it must be not lower than 87 - 90%. When the strength of the sulfuric acid is reduced below these limits, the nitration reaction does not occur at all, for all practical purposes.

A significant effect upon the nitration reaction is exercised by the nature of the attacking agent, reaction conditions such as the medium (Bibl.174), the temperature, and ~~and~~ other factors.

Depending upon the nature of the attacking reactant, and also upon the factors indicated, the molecules of certain substances may ~~may~~ manifest either electron donor or electron acceptor properties. Usually this manifestation of the

mutual influence of the atoms, which affects the susceptibility to redistribution
49 of electron density, occurs at the moment of chemical reaction and is termed
dynamic. Dynamic influence in the molecule is transmitted by the same methods
as is static influence, i.e., by a chain of simple bonds - as inductive influence,
or by a conjugate chain - as the effect of conjugation.

The dynamic redistribution of electron density under the influence of these
factors may have as consequence a change in orientation. For example, we know
that temperature (Bibl.175) affects the relationship between the resultant isomers,
as does the medium in which the reaction occurs (Bibl.176). An increase in
temperature upon nitration of toluene carries with it an increase in the yield
of the meta-mononitrotoluene, formation of which should not occur, as the CH₃ group,
which is an electron donor, reinforces the electron ~~XX~~ density of the ortho- and
para-carbon atoms, and thus ~~XXXXX~~ orients the entry of the NO₂⁺ cation into the
ortho- and para-positions.

Brown (Bibl.177) in a study of the toluene substitution reaction, introduced
the idea of the ~~XXX~~ existence of various degrees of "activity" of the attacking
particles, upon which there depends the relationship along the isomers formed. This
relationship frequently runs counter to the orientation determined by the substitute
groups already present.

Influence of the nature of the nitrating agent upon the chemical activity and
orientation has been revealed by A.I. Titov (Bibl.83, 98). Nitration begins with
complex formations as a consequence of the introduction of an electrophilic

atom of nitrogen of the nitrating agents into region II of the electrons of the ring in accordance with the mechanism



The formation of these complexes is accompanied by the appearance of a tint, the stability and depth of which is proportional to the readiness with which the corresponding aromatic compound ArH is nitrated (the coloration of the complexes becomes deeper, from colorless to ruby red, in the following sequence: benzene, naphthalene, anthracene).

The capacity of oxygen compounds of nitrogen NO_2X and NOX to undergo complex formation and the nitration reaction has to be determined both by the degree at which they are electrophilic, and by the degree to which the N atom is not saturated in terms of coordination. In an identical coordination number, the activity is determined by the electrophilicity, and the most active will be the free nitronium cation $\text{O}=\text{N}=\text{O}^{\oplus}$ solvation greatly reduces its activity. A.I. Titov explains the reduction in the selectivity of the nitro group entering the ring, upon increase in ~~XXXXXXXXXX~~ temperature, by reduction in solvation of the nitronium cation. The maximum activity will be ~~XXXXXXXXXX~~ displayed by NO_2^+ in the gas phase, when it reacts exceedingly rapidly and in all positions, and is not subject to the usual rules of orientation.

D. Effect of Temperature upon Nitration Reaction Velocity

Temperature is an important factor in nitration. With increase in temperature, the nitration reaction velocity rises, as is clearly evident from the data in Table 8. The temperature coefficient of the nitration velocity constant is

approximately three, i.e., a 10°C change in temperature is accompanied by a threefold ~~increase~~ increase in reaction velocity*.

Table 8

a)	K_{35}	K_{25}	$\frac{K_{35}}{K_{25}}$
b)	0.013	0.004	3.25
c)	0.47	0.18	2.61
d)	1.23	0.39	3.15

a) Substance; b) 4,6-dinitrometaxylene; c) ~~Meta~~ Para-chloronitrobenzene;
d) Meta-chloronitrobenzene

50 Nitration is, as a rule, accompanied by oxidation, and the velocity of this reaction varies ~~in~~ with temperature in approximately the same way as the velocity of the nitration reaction. However, the oxidation reaction demonstrates a peculiarity in that the oxidation products - nitrogen oxide - usually accelerate it, and therefore, as they pile up, the oxidation velocity rises progressively.

Inasmuch as the nitration reaction is exothermic

(the amount of heat emitted upon the entry of a single nitro group is 36.4 - 36.6 kcal/g-mole and, moreover, heat of hydration is emitted), therefore, on the

~~***~~
* Table 8 was compiled by Martinsen (Bibl.158) for homogeneous nitration conditions. Upon nitration in heterogeneous conditions, the temperature coefficient of the nitration velocity of the substances illustrated in the Table is lower as, under these conditions, the process governing the nitration rate will be the process of diffusion.

one hand, it is necessary, in a number of cases of nitration, to have recourse to external cooling of the apparatus, and on the ~~other~~ other hand to apply a continuous addition of nitrating mixture to the substance being nitrated.

For each compound and particular composition of the mixed acids, there is an optimum temperature, above which the oxidizing processes begin to go at a higher velocity, resulting in reduced yield of the substance produced, and which may even be the cause of an explosion or flare up if velocity proceeds to too high a level. In accordance with the introduction of electrically negative substitute groups (SO_3H ; NO_2 ; Cl) into the hydrocarbon molecule, the compounds become more stable in terms of processes of oxidation (the reaction capacity of the substances), and therefore nitration thereof may be performed at a higher temperature. However, the presence in the hydrocarbon of electrically positive substitute groups (CH_3 ; NH_2 ; C_2H_5) is the cause of the higher reactivity of these compounds, and consequently of their ready oxidizability. Compounds of this kind not only must not be nitrated at high temperature, but sometimes it is necessary, in order to reduce reactivity, first to introduce into the molecule an electrically negative substitute group such as SO_3H , and only then to proceed to nitrate.

As is evident from the foregoing, the temperature conditions of the nitration reaction have a major effect upon the behavior and results of the nitration reaction, and therefore require careful control and regulation.

E. Side Reactions ~~Accompanying~~ Accompanying Nitration

The yield of nitration products is 90 - 95% of the theoretical, but not infrequently it is considerably less than this. This is due to the fact that the

nitration reaction is accompanied by other processes, the most important of which is oxidation, which results either in the formation of products that are dissolved with comparative ease in the spent acids and water (substances containing the COOH, ~~the~~ OH groups), ~~or~~ ^{or} even to formation of gaseous products of complete oxidation.

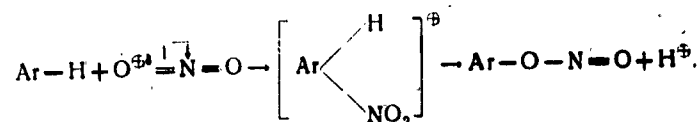
Thus, for example, ~~the~~ in the nitration of toluene, the nitro derivatives of benzoic acid and the destruction product of ^{the} benzene ring - ~~the~~ ^{tetranitromethane} - ~~are~~ are always formed. In the nitration of naphthalene, there is formed not only the nitration products but dinitronaphthol (from 0.5 to 3.5%) (Bibl.178). In the nitration of benzene, the formation of nitrophenols, and even of styphnic acid (2,4,6-trinitroresorcine) ~~is~~ has been observed (Bibl.179). In the nitration of the sulfate salt of dimethylaniline, one also observes the formation of 2,4,6-trinitro-3-oxyphenyl-N-methylnitroamine.

The mechanism of formation of products containing the OH group is not completely clear. It is held that the entry of oxy groups into the compound occurs at the outset in accordance with the usual laws of substitution, followed by nitration of the oxy compound. The oxy group is formed by reaction not of the nitrogen of the nitrating agents, but of its oxygen, with the aromatic compound, in accordance with the following mechanism (Bibl.98, 178)

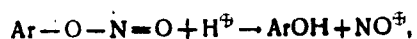


The oxy ~~compounds~~ ^{compounds} formed may be subjected to nitration, in which case the NO₂ group is directed into the ortho-position relative to the OH group. The number of side products of oxidation increases with increase in the sulfuric acid content of the nitro mixture.

According to A.I. Titov (Bibl. 98), oxidation in the nitrating mixture may also proceed ~~XXXXXXXX~~ via the nitronium cation. Inasmuch as in the nitronium cation $O=N=O^{\oplus}$ the electrons of the ~~XXXXXXXX~~ ^{peri-bond} are considerably displaced toward the cationoidal atom of nitrogen, the ~~XXXXXXXX~~ ^{nitrogen} atoms must also be strongly electrophilic in nature. Therefore, the attack by NO_2^{\oplus} upon the aromatic ring may be performed either by the nitrogen atoms or by ~~XXXX~~ ^{those} of oxygen:

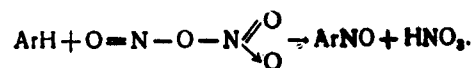


The aryl nitrate thus formed ~~XXXXXXXX~~ converts to phenol:

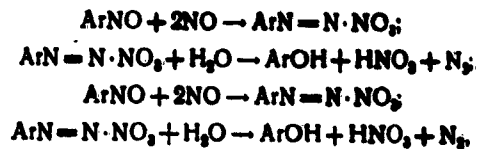


which is converted by the nitrating mixture into polynitrophenol.

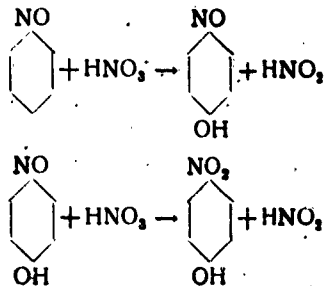
Formation of oxy compounds may also proceed from the stage of a nitroso compound, ~~XXXXXXXX~~ derived from the aromatic compound upon reaction therewith of ~~XXXXXXXXXXXX~~ the nitrosyl cation (NO^{\oplus}) or of a group ~~XXXX~~ containing it, such as nitrosyl sulfuric acid ($O=N-OSO_3H$) ~~XXXXXXXXXXXX~~ or the nitrosyl nitrate form of nitrogen dioxide $O=N-O-N \begin{array}{l} \diagup O \\ \diagdown O \end{array}$ by the mechanism



The nitroso compound may, further, under conditions of nitration in reaction with nitrogen oxide pass through the stage of a diazo compound to an oxy compound:

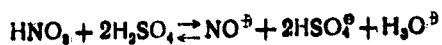


and, upon reaction with nitric acid, form para-nitrophenol:

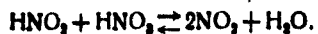


Then the phenols, as well as the para-nitrophenols undergo nitration to the ~~XXXXX~~ polynitro compounds (Bibl.70, 71). Thus, in accordance with the views of A.I.Titov, entry of the oxy group into the ring ~~XXXXXXXXXXXX~~ is facilitated by the presence of nitrogen oxides in the nitrating mixture.

52 The oxidizing processes are frequently so considerable that the consumption of nitric acid therein often attains 180 - 200% of that theoretically required for nitration. The oxidation process is accompanied by the formation of nitrogen oxides which, as already indicated, react with the compound undergoing nitration, converting it into a nitroxy compound. Moreover, in the nitration of a number of aromatic ~~XXXXX~~ compounds, the nitrogen oxides diminish the velocity of this reaction (Bibl.156), due to two processes: reduction of the strength of the sulfuric acid



and reduction of the strength of the nitric acid



In the case of strong oxidizing processes, as a consequence of which a considerable amount of nitrogen oxides are formed, nitration is substantially inhibited by this side reaction. However, the nitration of aromatic amines and phenols is promoted by nitrogen oxides, and thus the side reaction (oxidation), leading to formation of nitrogen oxides is, in the given instance, the cause of positive catalysis.

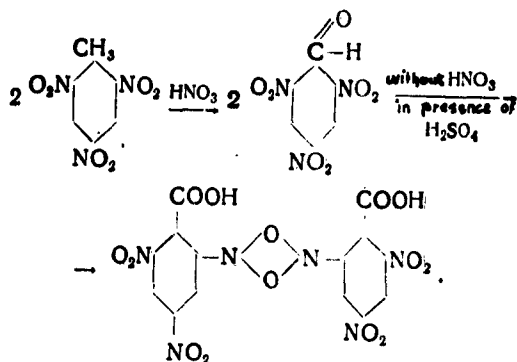
The catalytic effects of nitrous oxide is explained (Bibl.180) by the presence of a nitrosification reaction yielding nitroso compounds which are then oxidized to nitro compounds. Nitrosification is induced by the nitrosyl cation NO^+ or N_2O_4 . Although the latter are less active, the concentration thereof is considerably higher.

The nitrosyl cation is a considerably weaker electrophilic reactance than is the nitronium cation NO_2^+ . Therefore, it is only able to attack highly reactive aromatic compounds (such as the amines, phenols, phenol esters, etc.), and therefore it is only the nitration of these compounds that is promoted by nitrous acid.

In some cases, the formation of products ~~XXX~~ containing the nitroso group has been observed in nitration. Thus, in the nitration of toluene to trinitrotoluene, the formation of the dimer of dinitro-nitrosobenzoic acid occurs. It is held that this compound results from the oxidation, by nitric acid, of the methyl group to an aldehyde group, and subsequently, in the absence of nitric acid, by the

oxidation of the ~~XXXXXX~~ aldehyde group to the carboxyl group, this occurring ~~II~~

at the expense of the nitro group in the given molecule (Bibl.181):



53

In the nitration of aromatic hydrocarbons under certain circumstances, the entire mass is observed to become darker, resulting sometimes in the appearance of a flaky ~~black~~ ^{cherry-}black deposit. The degree of ~~XXXXX~~ darkening and the subsequent development of the process is far from identical in all instances. Sometimes the process is exceedingly vigorous, and the reaction mass begins to fume, and this not infrequently results in expulsion of nitro mass from the apparatus.

The formation of a black side product upon the nitration of benzene was first described by Battegay (Bibl.57), who observed this in nitration by nitric oxides in a sulfuric acid medium, and who drew attention to the dark and rather stable coloration of the spent acids. Disappearance of the colors set in only upon addition of water or nitric acid. Battegay assumed that the colored product is the complex consisting of benzene, nitrosyl sulfuric, and sulfuric acids:



According to a study by Ye.Yu.Orlova and S.S.Romanova (Bibl.182), toluene,

under these conditions, yields a complex of the following composition:



the formation of which facilitates an increase in the strength of the mixed acid, an increase in temperature, an increase in the content of nitric oxides, and a reduction in the strength of the nitro compounds.

Formation of the complex proceeds in two stages: darkening and, subsequently, foaming, as temperature increases, leading to the appearance of a black deposit, usually resinous. This complex is capable of being broken up by nitric acid. The stronger the acid mixture, the more readily this process will occur. In a weak acid mixture, the complex does not undergo destruction ~~EX~~ even when there is a large ~~EXCESS~~ excess of nitric acid. Consequently, destruction of the complex can be performed only by the nitrating form of nitric acid. Thus, the process of destruction of the complex of nitric acid resolves itself to a process of nitration of the hydrocarbon bound in the complex.

In order to avoid formation of a complex upon nitration of the aromatic hydrocarbon by mixed acid, it is necessary to eliminate the possibility that the hydrocarbon will come into contact with the spent acid free of nitric acid. However, if such conditions do arise and a complex is formed, steps must be taken immediately to destroy it. The work of Ye.Yu.Orlova and S.S.Romanova showed that destruction of the toluene complex should be performed at a temperature of 40 - 50°C. At this temperature the rate of destruction of the complex is higher than the speed at which it is formed. When the nitro mass darkens and the complex has not yet been broken, temperature must not be permitted to rise (specifically,

in the case of toluene, above 65°C). Otherwise, foaming will begin, and this will result in the formation of an ~~amorphous~~ amorphous brown substance. The initial stage of nitration is particularly dangerous in terms of the possibility of complex formation. Later, as the hydrocarbon is transformed into the nitro compound, this latter inhibits the formation of the complex.

Complex compounds of hydrocarbons with nitrosyl sulfuric acid are readily oxidized and resinified, as noted above, particularly at elevated temperature. The velocity of oxidation and resinification of the hydrocarbon is affected by its temperature. Benzene is most stable thereto. However, its homologs having substitute groups electrically positive ~~are~~ are less stable and oxidize at high velocity.

The stability of the hydrocarbon is the lower, the greater the number of substitute groups of this type in the benzene ring. The number of substitute groups being equal, the hydrocarbon ~~oxidizes~~ oxidizes the more rapidly, the lower is the chain of substitute groups. For example, ethyl benzene oxidizes more readily than does toluene.

54 The number of substitute groups being equal, oxidation velocity depends upon the relative position of the substitute groups. Those hydrocarbons oxidize most readily whose substitute groups are in the ortho-position with respect to each other; oxidation is more difficult where the para-position obtains, and the ~~meta~~ meta-substituted are the most stable. Thus, of the three xylenes, it is ortho-xylene in the trimethylbenzene series that oxidizes most ~~rapidly~~ rapidly. Pseudocumene oxidizes most readily, whereas mesitylene oxidizes with greater difficulty.

CHAPTER III

~~EXTRACTIVE SOLVENTS~~

NITRATION FLOW SHEET

A. Factors Governing the Nitration Flow Sheet

The optimum conditions for the production processes are determined by the ~~best~~ physical-chemical properties of the substances participating in the various stages of the chemical ~~process~~ transformations. These properties are basic to the choice of the condition to be maintained in the production unit, and the relationship among reactants, temperature, pressure, duration, the need for and possibility of employment of solvents, catalysts, etc.

The production processes involved in the synthesis of high explosives are carried out under various temperature conditions and common conditions for the reactants. In the majority of cases they are performed in liquid media (in a single liquid phase, in a mixture of two liquid phases, by reaction between liquid and gas, or between liquid and a pulverized solid), and this facilitates the decision and simplifies the design of the apparatus.

The basic process in high explosives synthesis - nitration - is accompanied by the emission of a considerable amount of heat due to the exothermic nature of the reactions occurring: ~~nitration~~ nitration, hydration, and not infrequently, oxidation. Therefore, as the process is usually conducted, if provision for withdrawal of heat is lacking, the temperature of the reaction mass rises to a specific level, whereupon, as the reaction velocity diminishes, heating diminishes

and the temperature begins to drop.

Inasmuch as nitration proceeds under a specific temperature conditions governed by the properties of the substances participating in the process, this temperature is maintained at the outset by cooling and toward the end by heating the reaction mass. Violation of the temperature conditions of the process may result in decomposition of the nitro product, often ending in a ~~XXX~~ flare up or explosion. A flare up or explosion is frequently the consequence of violation of the flow sheet and inability to determine in time the reasons for a sudden rise in temperature.

It must be borne in mind that explosives are dangerous only under specific conditions. The job of the technician is to be able to prevent these conditions developing under industrial circumstances.

The nitration flow sheet should be such as to assure ~~XX~~ maximum output and efficiency, i.e., maximum yield of the final product per unit of raw material. This is determined to a considerable degree by properly designed ~~XX~~ acid circulation. At the same time, a number of other conditions must also be met: an adequate margin of safety, and prevention of oxidizing and other side reactions.

Aside from the foregoing, the type and arrangement of ^{the} apparatus employed is also determined by the overall condition of the materials being processed. The apparatus employed must be designed simply and must be carried into compact and readily controllable installations.

55 Fulfillment of these conditions makes it possible to set up production that

will assure high labor productivity and low product cost.

Each method of production of polynitro compounds is characterized ~~by~~ by:

1) the number of stages of nitration; 2) the sequence in which the components are charged; 3) the nature of the acid circulation; 4) the processes cycle.

Section 1. The Stages of the Process

The affect of substitute groups in the benzene ring govern the changes in the conditions of nitration at various stages in this process. As nitro groups are introduced into the compound, their inhibiting influence upon the nitration velocity makes necessary the use of increasingly stronger acid mixtures. The consumption of acids in the production of polynitro compounds depends, to a considerable degree, upon the number of stages of the process.

The nitration process may be carried out in a single stage, in two stages - via the ~~intermediate~~ mononitro compound or the dinitro compound, in three stages, and in three stages with the ~~intermediate~~ subdivision of the last into a number of sub-stages.

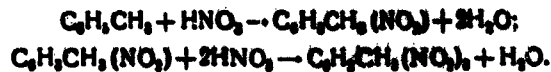
Nitration in a single stage as performed, for example, in the nitration of toluene, follows the following equation:



In this procedure, all the spent acid is diluted by the molecules of reaction of water and must be of maximum strength in order for the third nitro group to enter the ring. In this connection, the consumption of acids is at a maximum, and the acid mixture has to be made up of the mixtures of highest concentration: strong (oleum and ~~nitric acid~~ nitric acid). A considerable amount of the trinitro compound remains in solution in the large volume of strong spent acid, and this ~~substantially~~ ^{substantially}

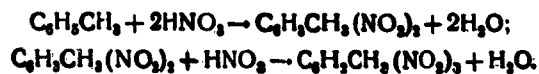
reduces the process output rate.

Nitration in two stages via the mononitro compound:



In this method, a weak mixed acid is used in the introduction of the first nitro group, and the strong mixed acid, which satisfies the requirements for the introduction of the third group is expended when the ~~second~~ ^{latter} two nitro groups are introduced. Therefore, this method is more profitable ~~than~~ than the first.

Nitration in two stages via the dinitro compound:



This method is more profitable than the preceding one, inasmuch as the strong mixture is employed only to introduce the third nitro group, and a weaker mixed acid is employed in the introduction of the first two nitro groups.

Nitration in three stages. Under this method, the strong mixed acid is expended on the introduction of only the third nitro group into the ring, a weaker is used to introduce the second nitro group, and a very weak mixture for the first. ^{The consumption} ~~consumption~~ of strong acids in this process is even less than in nitration by methods referred to above.

Nitration with separation of a third stage into several substages (phases).

Under this method, the consumption of strong acids is reduced even further. By breaking nitration up into a number of stages, it becomes possible, in the ~~first~~ first of these, to employ mixed acids of lower ~~strength~~ strength. Inasmuch as

the nitration in this case will proceed in the presence of excess compound undergoing nitration. It is ~~in~~ only the final stages that require ~~the~~ more concentrated mixed acids as the active mass of compound being nitrated is reduced.

Increase in the number of stages in nitration complicates the factory equipment and results in greater expenditure of labor. However, with a rational flow sheet, and successful design of the equipment, the number of stages in nitration can be increased considerably (Bibl.183). Separation of the process into a large number of stages is preferably reserved for the last stage (introduction of the third nitro group), inasmuch as the greatest amount of strong acid is required due to the difficulty of this process.

The degree of nitration may vary in the various stages. The process may be performed with adherence to precise molecular ratio among the reacting components, or without adherence to this precision. In the former case for example in introduction of the first nitro group, the entire hydrocarbon is nitrated to mononitro compound, in the second, to dinitro compound and upon introduction of the third, to trinitro compound. This flow sheet makes for ready monitoring of the intermediate products, for example, ~~in~~ imperfect products ~~are~~ noted immediately, etc., whereas when conducting the nitration in a number of ~~many~~ buildings, the purpose of each building is quite distinctive. The nitro product produced has various specific properties (physical-chemical constants and characteristics).

In the latter case, for example, upon introduction of the first nitro ~~in~~ group

in
~~XXXX~~ the first stage, toluene ~~II~~ undergoes only 50% nitration to mononitrotoluene
with the purpose of maximum utilization of nitric acid from the spent acid. In
the second stage, the process is conducted so that the nitro product obtained is
liquid at a temperature of 30 - 35°C, which is achieved when mixtures of nitro
products containing 50 - 75% dinitrotoluene and correspondingly 25 - 50%
mononitrotoluene are employed. The liquid nitro product is more readily separated
from the spent acid and it is then that nitration to trinitrotoluene is performed.

Section 2. Procedure of Charging of Components

In each of the methods of nitration listed above, the sequence of run-in of
the components may be different: ~~XXXXXX~~ ^{run-in} of the acid mixture to the compound being
nitrated ("direct" run-in), or run-in of the compound into the mixed acid ("inverse"
run-in), or, finally, simultaneous charging of the components. The first two
methods are suitable only to cyclic processes, whereas the third may be used in
continuous process.

The sequence in which the components are charged has a substantial effect
upon the cost and upon the result of nitration. Let us examine it, employing the
nitration of aromatic hydrocarbons of the mononitro compounds as ~~XXX~~ our example.

In "direct" charging of the components, the full quantity of hydrocarbon to
~~XXX~~ be nitrated in a single operation is run-in at once, followed by gradual addition
of the mixed acid. A special feature of this sequence of mixing of the components
is the presence of excess hydrocarbon during the nitration. ~~XXXXXXXXXX~~ ^{When} this sequence
is employed, the nitration/process ^{process} rate is ~~XXXXXX~~ low at the outset, because of the slow
addition of the mixed acid, and consequently ~~XXXXXXXXXX~~ ^{below} nitric acid content of the bath.

This latter circumstance may also result in a side reaction between the compound
57 being nitrated ~~XXX~~ (if there is no nitro group in the ring thereof) and the
nitrosyl sulfuric acid, resulting in the formation of the Battagay complex (Bibl.57)



Congruents of this kind are readily oxidized and ~~XXXXXXXXXX~~ ^{resinified,} particularly
at elevated temperature. Therefore, when the direct method of run-in is employed,
low temperatures must be maintained during the process.

As indicated above [pp.99 - 105(Bibl.182)], formation of the complex
facilitates an increase in the strength of the mixed acid, an increase in
temperature, and in the amount of nitrosyl sulfuric acid present. This last
circumstance is the major obstacle to the utilization of components of the
nitrating mixture from spent acid, in direct run-in, inasmuch as spent acids
almost always contain nitrosyl sulfuric acid.

In "direct" run-in of the components, the cooling surface of the apparatus
is inefficiently employed, inasmuch as the volume of hydrocarbon is usually less,
by a factor of two to three, than the volume of acid mixture.

The sole advantage of direct charging of the components, conditioned by the
presence in the apparatus of an excess of ~~XXXXX~~ nitratable compound, is the
possibility of producing pure mononitro compounds without admixture of dinitro
compound, and maximum utilization of ~~XXXXX~~ nitric acid to form the nitro compound
(Bibl.185). However, in the synthesis of polynitro compounds, the mononitro
compound is an intermediate product in further nitration, and therefore there is

no need to produce it in the pure form.

In the case of "inverse" run-in of the components, ~~IX~~ the entire acid mixture is charged into the apparatus, and then the hydrocarbon to be nitrated is added gradually as the nitration proceeds. A special feature of this method is the fact that excess nitric acid is present virtually throughout the nitration process. Under these circumstances of nitration, no complex is formed, inasmuch as the hydrocarbon is immediately converted, upon contact with the acid mixture, into a less reactive nitro compound, which neither ~~reduces~~ ~~nor~~ oxidizes. In "inverse" run-in, the end of charging of the components is readily determinable. So long as there is nitric acid in a mixture, it has a bright yellow color, but after the nitric acid has been consumed, the batch grows darker immediately because of the formation of the ~~colored~~ ^{colored} complex. "inverse charging", In ~~the process~~ the heat conditions of the process are more favorable.

A special feature of this process is the formation at the onset of nitration, of a dinitro compound (up to 10%) as a consequence of the fact that a strong admixture is employed, containing a large amount of nitric acid. Under circumstances in which the mononitro compound is an intermediate product in the production of di- and trinitro compounds, partial nitration to the diproducts in the first phase is actually desirable, as it reduces the consumption of the stronger acids in the second stage of nitration.

A process proceeds a good deal more smoothly in simultaneous charging of the components, which is usually employed when the continuous process is used. The

reactant components are run into an apparatus filled with spent acid. The capacity of the apparatus must be adequate to make it possible for the components to remain therein for the period of time required for the reaction to come to completion. Under these conditions there is no unnecessary excess of one of the components, and therefore side reactions are held to a minimum, and some of them are actually absent (for example such as the formation of the complex or the formation of a dinitro compound).

58 Section 3. Acid Circulation

In nitration of mixed acid, the sulfuric acid ~~XXXXX~~ is ~~XX~~ not consumed in the process of nitration, but is merely diluted with water and ~~XX~~ goes out of the process in the form of what is termed spent acid. In order to economize on sulfuric acid, the spent acids from the higher stages of nitration are employed, in multiple stage processes of polynitro compound production to make mixed acids for the lower stages of nitration. For example, the spent acid from the third stage goes partially or completely to preparation of mixed acid for the second stage, whereas the spent acid from the second stage goes to make mixed acid for the first stage.

This utilization of spent acids from the higher stages of nitration to make mixed acids for the lower stages of nitration is termed acid circulation. A rational acid circulation makes for minimum acid consumption factors and high yields and quality of product. Inasmuch as stronger acids are required for the higher degrees of nitration than for the lower, it is clear that the spent acid from the higher ~~XXXXX~~ stage of nitration may go to make the mix for the lower.

Thus, countercurrent between product and acid is rational in a continuous nitration ~~process~~ process.

In accordance with the nature of the acid rotation, the methods of conduction of nitro compounds may be classified as follows: acid circulation lacking, incomplete acid circulation, and complete acid circulation.

From the point of view set forth above, the method not employing acid circulation is rational only in a process in which it is not necessary that the procedure be broken down into various stages. In the multiple stage method (for example, in nitration of toluene through three stages), acid circulation was absent only in the earliest period of development of this method of production, ~~and~~ ~~and~~ and the acid mixtures for each stage of nitration were prepared from fresh acids, and the spent acids were ~~discarded~~ discarded.

The method employing incomplete acid circulation remains in use to this day in the two-stage method of nitrating ~~toluene~~ ^{xylene} to trinitroxylene.

Complete acid circulation, in which the spent acids from the higher stages of nitration are employed in their entirety to ~~make up~~ make up acid mixtures for the lower stages is the most profitable. With this method, not only is there a reduction in the total consumption of sulfuric acid, but there is also a reduction in the consumption of nitric acid ~~IX~~ as a consequence of its more complete utilization. Recovery of spent acid ~~IX~~ ^{upon} denitration is facilitated, as it emerges in the form of the most weakly spent acid from the first stage of nitration, containing 60 - 70% H_2SO_4 , and a negligible amount of nitro compounds.

Moreover, extraction of the nitric acid and decomposition of the nitrosyl sulfuric acid in denitration proceeds the more readily, the weaker is the sulfuric acid in which they are dissolved.

Where "direct" run-in of a mixed acid into the compound being nitrated is employed, acid circulation is permissible only under the condition that the spent acid be most carefully cleansed of the dissolved nitro products, if the spent acid is to be employed in making mixed acid. This is done by cooling the spent acid and settling it for a long time (up to 20 days). Otherwise, oxidation and resinification will go farther.

The situation is different in "inverse" run-in. In this procedure, there is always an excess of nitric acid, and the hydrocarbon charged is immediately converted to a nitro compound that does not react with the organic admixtures present in the mixed acid. Consequently, in inverse charging, it is not essential that the spent acids be cooled and settled if they are to be used to make mixed acid.

59 Therefore, the spent acids are sent directly from the separator to the lower-stage nitrator, mixed with nitric acid and nitration is begun with the mixed acid thus produced. This type of acid circulation is called hot. Its advantages are:

- 1) The ~~heavy~~ need for long-term preliminary settling of the spent acids, which requires large capacities, is eliminated;
- 2) The need for special acid-mixing apparatus is eliminated;
- 3) The acid department of the plant becomes simpler and more compact, and the number of workers is essentially reduced.

Most desirable of all is a closed acid circulation/ⁱⁿwhich the spent acid

leaving the nitration department is completely returned nitration after denitration and increase in strength. In this kind of acid circulation, the sulfuric acid required as a reaction medium is employed in production in a closed cycle, and it is merely a small amount of fresh sulfuric acid that has to be added in order to make good the losses.

Section 4. Production Cycle

In terms of the production cycle distinction is made between periodic processes of nitration (short cycle) and continuous nitration processes (long cycle, usually interrupted only to repair the apparatus, correct disturbances in the process, and for other such reasons).

The interrupted process is characterized by the fact that its various stages occur in a single place, and that time requirements vary. It is carried out in batch apparatus. In the periodic process, the final product is discharged from the apparatus at specific time intervals. After discharge, the initial components are charged into the apparatus and the production cycle is repeated.

The continuous process is characterized by the fact that all its stages occur simultaneously and that the end product is in a steady condition, with discharge continuous. It is performed in continuous-type apparatus. The continuous nitration processes are the more advanced. As a rule, they are considerably safer, readily subject to automation, require less ~~IX~~ labor, are more productive and economical.

^(A)~~IX~~ negative side of ~~IX~~ nitration in continuous apparatus is the fact that the nitration employs a mixed acid of minimal activity (the nitro batch in the apparatus is virtually spent acid), as a consequence of which reaction velocity

is low, but this in turn prevents spontaneous heating of the batch. Not infrequently, in order to achieve high output in the reactor, the reduction in nitration velocity (due to the low strength of the nitrating bath) is compensated for by ~~XX~~ running the process at high temperature. This last circumstance does not always have a favorable effect upon yield (losses due to oxidation), and also upon proper quality (for example, in the nitration of toluene, the yield of metanitrotoluene increases).

In continuous action apparatus, the problem of repair is more complex. In the repair of a single apparatus it is frequently necessary to stop others combined into a single continuous installation. Consequently, a good organization of maintenance work is essential in the operation of continuous installations. If monitoring is inadequate, it is possible that, in the continuous process, the
60 product will not be up to standard, and it is not always possible to rectify this.

The considerations set forth above must be borne in mind in deciding the type of cycle to be employed in nitrating any given product, inasmuch as, despite the theoretical advantages of the continuous process, the possibility that a batch process may prove more advantageous is not to be ruled out. Batch processes are employed chiefly in comparatively small installations, and in situations where satisfactory solutions have a problem of processes in continuous apparatus have not yet been found. Thus, the batch process must always be regarded as a transition stage to introduction of a continuous process.

Installation of continuous equipment creates the ~~EEEE~~ basis in materials and technology for ~~EE~~ raising labor productivity and reducing cost of production.

However, a superior process can only yield maximum economic effects if it is used correctly, rationally, and with skill.

B. Mixed Acids Employed in Nitration

Section 1. A Practical Description of Mixed Acids

The nitration of the majority of aromatic hydrocarbons is performed with mixtures of sulfuric and nitric acid. The relationship between the sulfuric and nitric acids in the mixed acid is set in such fashion that the nitric acid will go completely into nitration.

It was shown, in Chapter II, that the nitrating activity of mixed acid is determined by the ratio between the sulfuric acid and water. In the mixed acid, this ratio changes as the nitric acid is consumed in nitration, inasmuch as a molecule of water is liberated for each molecule of nitric acid consumed. In addition, the nitrating activity of the mixed acid is also changed. The ability of the mixed acid completely to yield the nitric acid it contains to nitration of the aromatic compound will be determined by the ratio between sulfuric acid and water in the spent acid. This ratio has come to be called the ~~dehydration~~ dehydration index (DI):

$$DI = \frac{\text{Quantity of H}_2\text{SO}_4 \text{ in mixed acid (\%)}}{\text{Amount of H}_2\text{O} \text{ liberated in nitration, plus amount of H}_2\text{O} \text{ in initial mixed acid (\%)}}$$

The value of the dehydration index of the acid mixture is determined experimentally.

Tomlinson and Groggins (Bibl.146) described the acid mixtures by a variant of the dehydration index, called the dehydration value of the sulfuric acid (DVS),

and computed in accordance with the following equation

$$DVS = \frac{S}{\frac{N}{N_r} (W \cdot W_p)}$$

including a coefficient for the consumption of nitric acid in nitration.

In this formula N_r is the nitrogen coefficient, which is arrived at as the product of the weight of the material undergoing nitration by the weight of the nitric acid required for nitration; S, N, and W are the percentage contents of H_2SO_4 , HNO_3 and H_2O in the initial mixed acid, and W_p is the amount of water liberated in nitration. They hold that at a given temperature and a given N_r , the product yield is a function of the DVS.

Considerably less ~~XXXXXXXXXX~~ ^{cumbersome,} more accurate, and, in our opinion, clearer, is the concept of the nitrating capacity of the mixture which characterizes it by the nitrating activity factor suggested by N.A.Kholevo (Bibl.127).

The nitric acid going into the mixed acid is not consumed in the nitration process, but only changes in strength as the nitric acid goes into nitration. Inasmuch as the utilization of nitric acid for nitration is accompanied by liberation of an ~~XXXXXXXXXX~~ equimolecular quantity of water, the strength of the sulfuric acid will be constant when the composition of mixed acid is described in molecular percentage.

The same relationship, as expressed in percentage by weight will be as follows, due to N.A.Kholevo:

$$S_1 = S_2 \frac{140 - N_1}{140 - N_2}$$

where S_0 and N_0 are the strength of the sulfuric and nitric acids in the acid mixture in percentage by weight, relative to the total weight of $H_2SO_4 + HNO_3 + H_2O$, and S_1 and N_1 are the concentrations of the same components in the middle or at the end of the nitration process. If ~~XXX~~ N_1 be taken as zero in this expression, then S_1 will take on some specific value, which N.A.Kholevo ~~is~~ ^{has} termed the liberating ~~IX~~ factor of nitrating activity of the mixed acid. The factor, termed f.n.a. may be computed in accordance with the following equation:

$$f.n.a. = S_c \frac{140}{140 - N_c}$$

The activity factor expresses the strength of the sulfuric acid on condition that the nitric acid ~~XXX~~ is completely used in the nitration process. His equation was derived as follows.

The weight of the spent acid after complete consumption of the HNO_3 upon nitration is

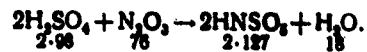
$$100 - N_c + \frac{18}{63} N_c = 100 - 0.714N_c$$

where 100 is the weight of the mixed acid, $\frac{18}{63} N_c$ is the weight of the water liberated in nitration, 18 and 63 being the molecular weights of the water and the nitric acid respectively.

The strength of the H_2SO_4 in the spent acid or

$$f.n.a. = \frac{S_c \cdot 100}{100 - 0.714N_c} = \frac{140 \cdot S_c}{140 - N_c}$$

According to this equation, one may compute the maximum nitrating activity of the acid mixture only if it contains no nitrogen oxides. When the spent acid is used to make mixed acid, nitrogen oxides will generally be present. Nitrogen oxides go into a compound with sulfuric acid, combining to form nitrosyl sulfuric acid, with liberation of water:



Reaction of one part of N_2O_3 per weight takes up H_2SO_4 as follows

$$\frac{2.98}{76} = 2.58 \text{ parts by wt.}$$

~~XXXXXXXXXX~~
and the H_2O liberated is

$$\frac{18}{76} = 0.24 \text{ parts by wt.}$$

and the HNSO_5 is

$$\frac{2.127}{76} = 3.34 \text{ parts by wt.}$$

62 it is
In computing the factor of nitrating activity/necessary to proceed from the active composition of the mixture, i.e., the composition less inactive matter.

Therefore, the formula for computation of the F.n.a. will be as follows:

$$f.n.a. = \frac{100(S - 2.58a)}{100 - 3.34a + 0.24a - 0.714N} = \frac{100(S - 2.58a)}{100 - 3.10a - 0.714N}$$

where a is the N_2O_3 content in the acid mixture, in percent.

This last equation may be employed in production to compute the F.n.a. in the spent acid on the results of analysis. The spent acid usually contains a dissolved nitro product, the content of which is taken into consideration in

computing the F.n.a., the formula in this case having the following appearance:

$$f.n.a. = \frac{100(2 - 2.56a)}{100 - 3.34a + 0.34a - 0.714N_2 - b}$$

where b is the nitro product content in the spent acid, in %.

Thus, the factor of nitrating activity for the initial mixed acid and for the spent acid obtained after utilization of this mixture is identical only if oxidizing processes have not occurred in the course of nitration. However, if oxidizing processes did occur during the nitration, a portion of the sulfuric acid will be taken up by the nitrogen oxides liberated therein to form nitrosyl sulfuric acid. This reduces the factor of nitrating activity of the spent acids.

In terms of the activity of mixed acids, the following are valid: 1) of two or more mixtures having identical factors of activity (F.n.a.), the more active at the outset will be the one in which the concentration of nitric acid is higher; 2) of mixed acids having identical nitric acid concentration, the more active ~~will~~ will be the one in which the factor of activity is the higher.

The characterization of mixed acids by ~~the~~ factor of nitrating activity, due to N.A.Kholevo, has had a very favorable effect upon the development of the manufacture of a number of polynitro compounds primarily TNT. It has demonstrated that mixed acids of various compositions may be used, provided that ~~their~~ their F.n.a. is identical. This in turn, has solved the problem of employment of spent acids for the preparation of mixed acids.

Section 2. Consumption of Acids for Nitration

The amount of nitric acid going to make up the nitrating mixture is determined by the amount theoretically required for nitration in accordance with the stoichiometric reaction equation



To the quantity of nitric acid found in this manner, there must be added a fraction thereof specific ~~XXXXXX~~ necessary to cover the nitric acid ~~XXXXXX~~ consumed in oxidation, evaporation losses, and residue in the spent acid. This excess is ~~XXXXXX~~ usually determined experimentally for each specific case.

The determination of the consumption of sulfuric acid required in nitration is another matter. This problem is facilitated if the limiting factor of nitrating activity required to obtain a given degree of nitration of the initial ~~XXXXXX~~ compound is known. Table 9 presents the F.n.a. values employed in practice, and the practical consumption of nitric acid as percentage of the theoretical required for nitration of the most important aromatic compounds.

The employment of acid mixtures, the spent acid of which will have an F.n.a. higher than that required to nitrate the given substance, is unprofitable in terms of sulfuric acid economics. The use of acid mixtures of low F.n.a. results in incomplete utilization of the nitric acid in this mixture. If we know the F.n.a., it is not difficult to determine, for each specific instance, the amount of sulfuric acid required to carry out the nitration process.

Let us use G_N to indicate the quantity, in kilograms, of nitric acid at a strength N (%) ~~XXX~~ of HNO_3 , and let us employ G_s to denote the quantity, in

64 nitration ($G_S \frac{S}{100}$) to the amount of spent acid:

$$f.n.a. = \frac{G_S \cdot S \cdot 100}{100 \cdot G_S + G_N (100 - 0.714N)} [\%],$$

from which

$$G_S = \frac{f.n.a. \cdot G_N (100 - 0.714N)}{(S - f.n.a.) 100}$$

or

$$G_S = \frac{G_N \cdot f.n.a.}{140} \left(\frac{140 - N}{S - f.n.a.} \right)$$

If we use this equation, we are in a position readily to compute the amount of sulfuric acid required to make up the mixture.

It is evident from the formula that the consumption of sulfuric acid is determined to a considerable degree by the difference between the concentration of H_2SO_4 in the sulfuric acid employed for nitration (S) and the concentration of H_2SO_4 in the spent acid (f.n.a.). As a consequence of the high value of the f.n.a., particularly in the nitration of dinitro compounds, it is necessary to employ sulfuric acid of ~~100%~~ maximum strength (not infrequently containing free SO_3) to make the mixed acid. However, even under these conditions, the consumption of sulfuric acid is considerable, and sometimes several times as large as the consumption of nitric acid.

The formula also shows that the composition of the acid mixture may change considerably in accordance with the concentration of the initial acids employed to make up the mixture. At maximum concentration of the initial acids, the

consumption of sulfuric acid will be minimal, and the percentage content of the nitric acid in the acid mixture will be at a maximum. On the other hand, if the initial acids are weak, the strength of the nitric acid in the acid mixture will be minimal. In such mixed acids, it is only the ~~initial~~ ^{final} nitrating activity that will be identical, whereas the nitrating activity of the initial mixtures differ.

The initial nitrating activity of acids ~~initial~~ containing much nitric acid will be greater and, consequently, the nitration velocity by these acids at the beginning of the process will be higher. This is of significance only for batch-type processes, in which the compound to be nitrated is run into the mixed acids. Nitration in continuous process apparatus has a rule (particularly for readily nitratable compounds) occurs in point of fact with mixed acids of nearly maximum composition. Upon continuous nitration in a nitrator, the mixed acid and the compound undergoing nitration are measured ~~in~~ ⁱⁿ simultaneously, often at a rate close to the speed at which they react. Under these conditions, the nitrator is filled with a nitro batch consisting of nitro products and the ~~in~~ nitrating mixture, similar in composition to spent acid. Consequently, in the case of continuous processes, the characterization of the acid ~~initial~~ ^{mixture} on the basis of maximum nitrating activity F.n.a. will be the most accurate.

It follows from the foregoing that in continuous processes, the employment of acid mixtures composed of weak acids instead of mixtures composed of strong, has no significant affect upon the nitration velocity. At the same time, compounding the mixed acids of weak initial acids is often economically advantageous. For example,

in multiple-stage nitration, it permits the use of the spent acid of the higher stages of nitration to prepare mixed acids for the lower stages of nitration.

65 C. Apparatus

Nitration is the major stage in the production of explosives of the nitro derivative class. It includes two major processes: nitration as such, and separation of the derived nitro product from the spent acid. Below we examine the specifications that have ~~XXX~~ to be met in designing the principal types of apparatus employed in these processes.

Section 1. Nitrators

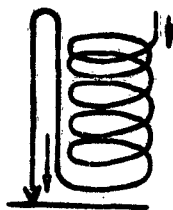
The nitration reaction is carried out in apparatus termed nitrators. These apparatus are made in a ~~XXX~~ ^{great} variety of designs, but they all have ~~XXXXXXXX~~ ^{to satisfy} specific requirements determined by the nature of the reaction occurring.

The nitrator design must be sufficiently simple, it has to be accessible to inspection and convenient for servicing. This is particularly important for apparatus in which the resultant nitro compound is of inadequate stability in its unpurified form. Long-term retention of this product ~~in~~ in parts of the apparatus inaccessible to inspection may result in decomposition of the product and accidents.

A nitrator employed to produce nitro compounds having explosive properties must have a drainage outlet of adequate cross-section, for connection with an emergency reservoir. The ~~XXX~~ drainage cross-section must be such as to permit the contents of the apparatus to be dumped into the emergency tank very quickly

conditions,
In order to maintain the required heat ~~XXXXXXXXXX~~ the nitrator should have
adequate surface area for heat exchange. This is usually achieved by means of

The coils ~~XXXX~~ are the most sensitive ~~parts~~ of the



apparatus. They go out of order rather easily, as
a consequence of corrosion. Entry of water from

the coil into the nitro mass may result in an

accident due to the sudden temperature jump as a

Fig.5 - Diagram of Cooling
Coil of Nitrator (showing
direction of water in the
coil)

consequence of heating of the contents by the ~~XXXX~~ ^{heat}

of nitration, and boiling up, or, under the most

favorable conditions, in ~~XXXXXXXXXX~~ ^{expulsion} of the nitro mass

from the apparatus. Not infrequently, coil leakage is the cause of a fire or even
an explosion.

To avoid accidents, coils must be examined periodically. It is desirable that
the delivery of water into the coils be by suction. This may be achieved by, for
example, placing the tube that removes the water at a level significantly below that
of the coil (Fig.5). If, with such an arrangement, the line into the coil forms
an ~~XXXX~~ aperture, what will occur at first is only a suction of nitro mass into the
coil. In accidents, nitrogen oxides are released from the funnel accepting the water
emitted from the coil. A much more reliable arrangement would be to transmit the
coolant water through the coil by means of vacuum or a centrifugal pump.

Not infrequently, as a consequence of the high nitration velocity of certain
compounds and, consequently, of the considerable amount of heat emitted in unit
time as it occurs, the output capacity of the nitrator will depend upon its heat

data. The output rate of nitrators under these conditions are proportional to the amount of heat that can be withdrawn from the reaction batch in unit time. In this situation, it is desirable to have nitrators of a design that would provide maximum coolant ~~EM~~ surface area.

Sometimes ~~EX~~ recourse has even^{been} had to the provision of additional coolant surface areas beyond those within the apparatus (for example, as a combination of coil and jacket). ~~XXXXXXXXXX~~ Condensers or tubes extending beyond the nitrator ~~XXXXX~~ shell may serve as such surfaces. To increase the withdrawal of heat, cooling is very often accelerated by special brines cooled to low temperature. This is ~~EM~~ apparently more desirable than additional coolant surfaces, and is frequently engaged in in the manufacture of explosives.

In order to provide rapid contact between the components delivered into the apparatus, intensive agitation is required. Towards this end, nitrators are equipped with propeller or turbine type mixers. Other types of ~~XXXXXXXXXX~~ mixing may be employed. Intermixing is also necessary in nitration to achieve more intensive and uniform heat control from the entire nitro mass in the apparatus.

The apparatus ~~XXXXXXXXXXXXXX~~ must contain no stagnant zones, as local ~~XXXXXXXXXX~~ overheating of the nitro mass due to inadequate ~~EX~~ withdrawal of heat may occur therein. Such an overheating may lead to the sharp increase in the velocity of the ~~XXXXXXXXXX~~ principal and the side reactions, and this is highly dangerous. Intensive stirring upon nitration in a heterogeneous medium also facilitates an increase in the speed with which the process goes.

The material used to build the nitrator is chosen on the basis of the properties of the reactance it will contain. In nitrating aromatic hydrocarbons by mixed acid of high concentration, containing no more than 20 - 25% water, the nitrator may be made either of cast iron or standard steel. Should mixed acids of lower strength, or pure nitric acid, or mixtures of the latter with acetic

acid be employed for nitration (for example, in the production of hexogen), the nitrator is made of special stainless steel or some other acid-resistant material.

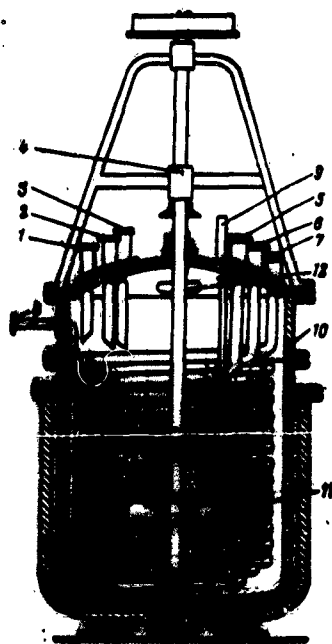


Fig.6 - Batch-Type Nitrator

- 1,2,3 - Entry ranges for component pipe lines;
- 4 - Agitator shaft bearing;
- 5,6,7 - Intake flanges for coolant water;
- 8 - Overflow flanges;
- 9 - Thermometer;
- 10 - Shell;
- 11 - Agitator propeller;
- 12 - Hatch

A thermometer is provided for purposes of following temperature conditions. The nitrator must have a device for removing the gases and vapors developed during nitration.

As we see from Fig.6, the nitrator is provided with coil and jacket. In the given instance, the coil has the purpose of delivering coolant water, and the jacket serves to deliver steam additional if ~~additional~~ heat is required. Heating

of the nitro mass is sometimes necessary at the end of the nitrating process, when the heat of reaction is inadequate to maintain the temperature required, as a

consequence of the low strength of the reactant components. The steam may also be delivered into the coil, in which case one may dispense with the jacket, as the latter makes it difficult to examine the shell from without.

A propeller-type agitator is suspended on bearings from a frame. The agitator shaft is provided with an oil-trap to prevent lubricant from entering the nitrator. This would result in combustion if the nitro mass contains acids of high strength. The agitator shaft passes through the cover via a hydraulic seal filled with 93% sulfuric acid. The inspection hatch in the cover of the apparatus also has a hydraulic seal filled with the same substance. The hatch, which is not battened down, facilitates safety in the operation of the nitrator. If oxidizing processes accompanied by the emission of gaseous products arise or become intense in the nitrator, the increase in internal pressure due to the accumulation of these products beneath the cover is eliminated, as these products lift the ~~XXXXX~~ hatch. This facilitates prevention of accidents, particularly when nitro products burn in the apparatus.

Section 2. Equipment for Separating Nitro Products from Spent Acids

After nitration, the nitro product produced has to be separated from the spent acid. The design of the apparatus used for this purpose varies widely. The difference in principle among these designs is determined by the joint state of the ~~XXXXXXXXXX~~ ~~XXXXXXXXXXXX~~ components to be nitrated. If the nitro product is liquid and is of a specific gravity different from that of the spent acid, it may be separated from the spent acid by the settling. If the nitro product is a solid, separation of

the spent acid is by filtering or squeezing out.

Separation of the products by settling is carried out in separators of various designs. These apparatus have to assure good separation at maximum speed. An increase in separation speed is ~~XXXXXX~~ facilitated by reduction in thickness of the layers, increase in the temperature of the mass being separated, etc. The separation speed is highly dependent upon the separator design. In some separators, shells are provided ~~interiorly~~ ^{in the interior} to reduce the thickness of the layers. Separators employing centrifugal force are also adducive.

Solid nitro products are separated from spent acid by filtering over ~~XXX~~ funnels or centrifuging, with the use of vacuum or pressure filters. Safety requirements are also taken into consideration in making the choice of apparatus. For example, highly sensitive explosives ~~XXXXXX~~ ^{must not} be separated from the spent acid on centrifuges. The use of pressure filters is dangerous if the substance is of reduced stability in the unpurified ~~XX~~ condition (for example as is the case with PETN). ^{Ignition} ~~XXXXXXXXXX~~ of these substances under pressure may result in explosion.

D. Control of the Nitration Process

In the chemical industry as a whole, and in explosives manufacture particularly, production control is of decisive significance. Correct conduct of the technological process makes for safety, assures the required quality of products and permits reduction in consumption of power and raw materials.

In controlling the nitration processes, much importance attaches to temperature readings, inasmuch as temperature is the major factor governing the product yield and, what is most important, safety in the process. Also important is observation of

and checking the condition of the medium in which the reaction occurs. One of the most important manifestations of proper process course are the characteristics of the intermediate products and the end products: specific gravity, freezing temperature, or melting point.

68 Recently, particular attention has been given to the problem of automation of the monitoring of production. In addition, the problem of automatic control has been advanced. This is particularly pressing and important for fields of manufacture in which explosion is possible or which are harmful to human health, as is the case with the manufacture of explosives. Automatic regulation of the process makes for optimum conditions of apparatus function, and this results in increase in apparatus capacity, and an improvement in the quality of the product, and a reduction in indices of consumption.

In automating the production of explosives and selecting the corresponding monitoring instruments, it is necessary to take into consideration the explosion danger and the degree to which the reactants exercise corrosive effects. Moreover, such fundamental processes (which are also those ~~most~~ most in need of automation) as nitration are rather complex in terms of monitoring inasmuch as they include not only the problem of observation of temperature, but determination of the composition of the mixed acid and the product undergoing nitration. Therefore, the first step in the direction of complete automation has to be automation of individual processes, which create the basis for general automation. ^{(It} ~~is~~ appears that the process of automatic monitoring and regulation of temperature will be the simplest to solve.

Various literature data indicate that the problem of automation of the production explosives is being given much attention. Thus, a description (X) (unfortunately, very brief) of a wholly automated process for the production of nitroglycerin (Bibl.186) has appeared. This example demonstrates that automatic monitoring and control over the process flow in the manufacture of explosives is entirely a realistic objective.

CHAPTER IV
ACID PROCESSES

A. General Description of the Acids Employed in Nitration

The ~~XXXXX~~ consumption of acids in nitration exceeds considerably the consumption of the starting compound, in explosives manufacture. Table 10 presents data with respect to the approximate consumption of acids per ton of certain (civil engineering) basic ~~XXXXX~~ explosives (Bibl.183).

Table 10

a)	b)				
	c)		d)		
	e)	f)	g)	h)	i)
j)	1500	1300	—	250	700
k)	—	1800	—	1130	—
l)	—	4700	—	2750	—
m)	—	—	10 000	—	—

a) Explosive; b) Consumption computed as monohydrate in kg; c) Sulfuric acid; d) Nitric acid; e) Oleum, with 20% SO₃; f) Commercial sulfuric acid 93%; ~~g) Nitric acid~~ g) Strong acid (98% HNO₃); h) Mixed acid (not less than 87% HNO₃ and 7.5% H₂SO₄); i) Weak acid (55% HNO₃); j) TNT; k) Dinitronaphthalene; l) Tetryl; m)RDX

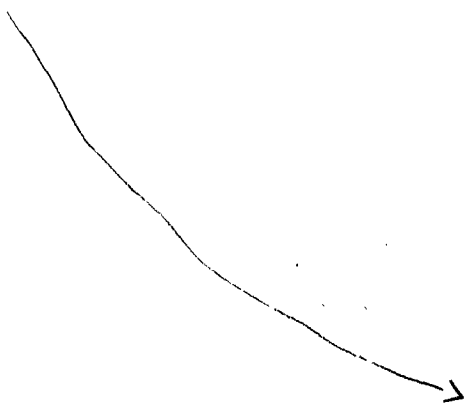
A large volume of spent acids containing sulfuric acid primarily are obtained as production by-products. The spent acids are preworked and recycled.

The consumption and circulation of acids at explosive plants exceeds severalfold the volume of finished products. Even if enterprises of ~~the~~ this kind have their own acid-producing enterprises, the nitration shops have to have large reserves of

production. In acids so as to assure no interruptions in ~~XXXXXXXXXX~~ this connection, the necessity arises for storage and special provision for receiving acids from suppliers. Other auxiliary ~~XXXX~~ shops are necessary, to perform such functions as the purification and processing of the spent acids. This system in its totality is termed the acid department of the enterprise. It includes absorption installations to trap vapors and gases emerging from the nitrators.

The basic chemical industry and the acid shops of explosive plants offer sulfuric and nitric acid of particular ~~XXXXXX~~ grades, corresponding to specific requirements, for sale. These specifications are governed rigidly, on the one hand, by conditions of production and transportation and, on the other hand, by the conditions of utilization both by the chemical industry and by ~~XXX~~ the explosives industry.

Pure 100% sulfuric acid (monohydrate) is a heavy oily liquid with a specific gravity of about ~~XXXX~~ 1.8356 at 15°. When water is added so that the strength becomes 97.25%, specific gravity rises 1.8415, but a further increase in the amount of water results in a reduction in specific gravity. The monohydrate begins to boil at 290°, decomposing into SO₃ and H₂O, whereas 338°, a continually boiling mixture (azetrope) containing 98% H₂SO₄ and 2% H₂O is formed.



When the monohydrate is saturated with sulfuric anhydride, fuming sulfuric acid results. A major component of fuming sulfuric acid, or oleum, is pyrosulfuric

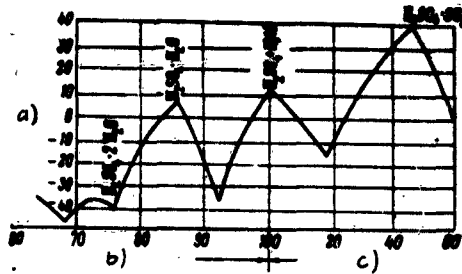


Fig.7 - Relationship of Temperature of Solidification of Sulfuric Acid to Its Composition

a) Solidification point in °C; b) H_2SO_4 contents, %; c) SO_3 content, %

acid $H_2S_2O_7$, which may be regarded as a solution of sulfuric anhydride in sulfuric acid monohydrate. The composition is therefore expressed in percentage of anhydride. The specific gravity of oleum increases with increase in SO_3 content up to 30%, but diminishes thereafter.

The solidification temperature of sulfuric acid is a function of its composition or, to be more exact, of the content of water of free sulfuric anhydride. As is evident from the curve (Fig.7), the freezing point of commercial sulfuric acid, i.e., of 75% strength, 92% H_2SO_4 , 20% SO_3 (oleum) is lower than that of acids of somewhat greater or lower strength.

Thus, the requirements that have to be met by sulfuric acid are also determined by conditions of transportation, particularly in the areas in which the ~~XXXX~~ and ~~XXXX~~ are cold. Acids at other strengths would more frequently present the problem of ~~XXXX~~ freezing in the tank cars in transportation.

The effect of sulfuric acid upon metals varies, depending upon its strength. ~~THE~~ Weak sulfuric acid very readily erodes (dissolves) iron, but does affect lead, as, on the contrary, strong sulfuric acid attacks lead readily, but has no effect upon iron. This difference in the effect of sulfuric acid in various strengths is

acid composed of 68% HNO_3 and 32% H_2O boils without decomposition at 120.5° , yielding an azeotrope.

As distinct from sulfuric acid, nitric acid has a considerably lower freezing point, which permits its storage in unheated buildings even in the northern portions of the country. Weak solutions alone represent an exception to this. Figure 8 shows the variation in freezing point versus strength.

Virtually all metals dissolve in nitric acid. Aluminum is stable to strong nitric acid (over 80%). High temperature, and admixture sulfuric acid increase the solvent action of nitric acid upon aluminum. As distinct from the pure metals, there is a large number of alloys that are stable to nitric acid. These are chiefly ~~XXXXXXXXXXXX~~ chromium-nickel steels of various grades.

The ability of nitric acid to corrode may be reduced by adding sulfuric acid to strong nitric acid. The addition is efficient if ~~XXXXXXXXXXXX~~ the sulfuric acid constitutes not less than 7% of the nitric acid and there is no more than 5% water in the mixture. This mixture (melange) can be stored in iron apparatus.

B. Transportation and Storage of Acids

Acids may be transported either in special or ordinary railway tank cars. Oleum, commercial sulfuric acid, and melange are transported in ordinary steel tank cars, whereas strong nitric acid is transported in chromium-nickel or aluminum tank cars.

Upon arrival at the plant, the tank cars are ~~XXXXX~~ delivered to the acid department.

The acid department includes storage for fresh acids, a device for emptying the acids from the railway tank cars, agitators, measuring equipment, vacuum installations for

charging the syphons, a pumping station, mixing kettles, storage for the nitre mixture and the spent acids, and a testing laboratory.

The acid is drained from the tank cars after analysis has been made and only if the acid arriving at the enterprise satisfies the specifications. The acid is emptied through the filler flanges by syphoning, because tank cars for acid haulage are usually not provided with bottom drains. The syphon is filled either from a special primer pressure tank or by pump. In the latter alternative, the receiving tank must be lower than the tank car bottom. Emptying may also be done by vacuum.

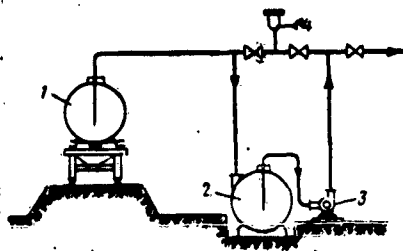


Fig.9 - Emptying Acids by Syphon
with Pressure Tank

1 - Tank car; 2 - Receiving tank;
3 - Pump; 4 - Pressure tank

Figure 9 illustrates the procedure for emptying the acid by syphon primed from a pressure tank having a permanent reserve of acid. This tank is filled ~~EX~~ by the same pump that serves to transfer the liquid from the receiving tank to the storage reservoirs. Priming of the pump may also be done from the pressure tank. Because of the difference in levels between the tank car and the receiving tank, the liquid is then transferred by gravity.

Figure 10 shows the method of emptying acid from railway tank cars by means of a syphon filled by pump, serving simultaneously to transfer the acid from the receiving tank to storage. In this arrangement, the receiving tank must always retain ^a ~~the~~ quantity of acids sufficient to fill the syphon.

Figure 11 illustrates the emptying of acids from railway tank cars into a receiving tank under vacuum.

After the receiving tank has been filled with acid, the tank is always emptied by pump into the storage reservoir.

The emptying of oleum is more complicated in winter time, because it freezes at -11°C (20% oleum) in the tank car, when shipped by rail. Frozen oleum may be

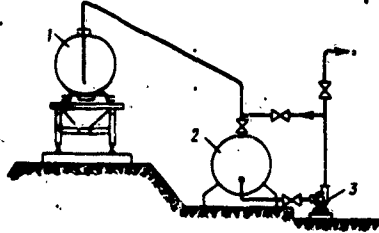


Fig.10 - Emptying Acids by Siphon

and Pump

1 - Tank car; 2 - Receiving tank; 3 - Pump

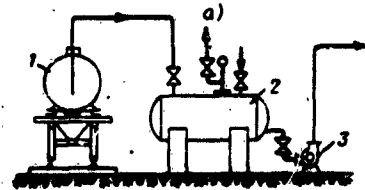


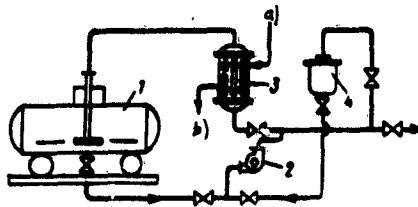
Fig.11 - Vacuum Emptying of Acids

1 - Tank car; 2 - Receiving tanks; 3 - Pump

a). Vacuum

emptied in one of several ways. One ~~method~~ consists of placing the tank car into a special steam-heated structure. The tank car remains in the structure until the entire frozen mass of oleum has melted, whereupon it is then drained by one of the methods

indicated above. This method is uneconomical because of the large amount of steam that has to be expended. Moreover, the tank car must sometimes remain in the heated structure for a period of days.



72 Fig.12 - Diagram of Circulation Thawing
of Oleum

1 - Tank car; 2 - Pump; 3 - Heater;

4 - Pressure tank for thawed oleum

a) Steam; b) Condensate

A more practical procedure is the circulation method of heating the oleum (Fig.12), performed by sending preheated oleum (1500 - 2000 ltr) into the tank car. Its

heat causes a portion of the frozen oleum to melt. This melted oleum is removed by pump, driven through a heater, and returned to the tank car, until all the oleum therein has melted, whereupon the pump is switched to delivery of the oleum into the storage collectors, and the tank car is emptied.

Acids capable of freezing during the cold season of the year (oleum, 96% commercial sulfuric acid) are stored in heated buildings.

6. Calculation of Acid Mixtures

Mixed acid for nitration may be made either from fresh acids or mixtures thereof, or from spent acids. Calculation of the mixed acids, particularly when three-component initial mixtures are employed, is rather complex arithmetically. It is much simpler to solve this problem analytically or graphically. Nomograms must be available if the latter method is to be used. ~~XXX~~

The analytical method of computing mixed acids by compiling balance equations.

Let us assume that it is necessary to prepare an acid mixture of $N\%$ HNO_3 , $S\%$ H_2SO_4 , and $W\%$ H_2O , in the volume of G kg, consisting of three initial mixtures:

	$\text{HNO}_3\%$	$\text{H}_2\text{SO}_4\%$	$\text{H}_2\text{O}\%$
first mixture	n_1	s_1	w_1
second mixture	n_2	s_2	w_2
third mixture	n_3	s_3	w_3

In order to obtain G kg of mixed acid, one needs x kg of the first initial mixture, y kg of the second, and z kg of the third. The sum of the weights of all the components of the required mixture is ~~XXXXX~~ equated to the ~~XX~~ weight of the mixture to be prepared (a weight equilibrium equation)

$$x + y + z = G \quad (1)$$

The amount of nitric acid monohydrate that will be in the mixed acid in preparation

is expressed by the following equation (nitric acid balance equation)

$$x \cdot n_1 + y \cdot n_2 + z \cdot n_3 = ON, \quad (2)$$

the amount of sulfuric acid ~~XXXXXXXX~~ (sulfuric acid balance equation) is

$$x \cdot s_1 + y \cdot s_2 + z \cdot s_3 = OS \quad (3)$$

and the amount of water (water balance equation) is

$$x \cdot w_1 + y \cdot w_2 + z \cdot w_3 = CW. \quad (4)$$

When we have jointly solved eqs.(1) - (4), we can determine the weight of the components.

Inasmuch as, in practice, mixed acids are usually prepared from individual acids, and not from mixtures thereof, this computation is considerably simplified.

Graphic method of calculating mixed acids. In the Gibbs triangle (Fig.13), the vertices represent one hundred percent content of the respective components, the sides represent binary mixtures, whereas an infinite number of acid mixtures of ternary composition ~~XXX~~ lies within the triangle.

Assume that the problem is to prepare a mixed acid of the required composition D

from the initial acid mixtures A, B, and C. If we join the points corresponding thereto, A, B, and C, we obtain a triangle within which lies point D. If, from the vertices A, B, and C, we draw transversals Aa, Bb, Cc, we obtain point D.

The segments Da, Db, Dc are termed the basis of the transversals. We ~~XXXXXXXX~~ know from geometry that the sum of the ratios of the basis of ~~XXXXXXXXXX~~

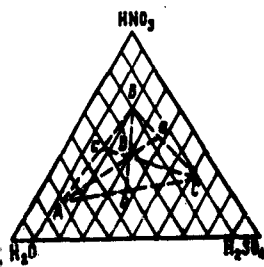


Fig.13 - Gibbs Triangle for Computing Mixed Acids

transversals to the transversals themselves equals unity, i.e.

$$\frac{D_a}{A_a} + \frac{D_b}{B_b} + \frac{D_c}{C_c} = 1,$$

where $\frac{D_a}{A_a}$ is the share of the first initial mixture;

$\frac{D_b}{B_b}$ is the share of the second initial mixture;

$\frac{D_c}{C_c}$ is the share of the third initial mixture.

XX If point D lies on one of the sides of the triangle ABC, it means that the acid mixture of ~~XX~~ the required composition may be prepared from the two initial acid mixtures alone. However, if point D lies outside triangle ABC, this means that an acid ~~XXXX~~ mixture of the required composition ~~XXXX~~ cannot be obtained from the given acid mixtures.

As we see, the graphic method is simple and obvious. A shortcoming is its relatively low accuracy. Therefore, it is desirable that this be used merely for control and for rough computation.

D. Preparing the XX Mixed Acids

Every explosives plant acid department has an installation for the mixing of acids. This installation includes equipment for metering, mixing, ^{and} storing the ready acids.

The mixer must be ~~XXXXXXXXXXXX~~ such as to assure an adequate degree of mixing and must have a cooling surface to remove the heat emitted as the acids are agitated. When sulfuric and nitric acids are mixed together, the temperature must not be allowed to rise beyond 40°C. Higher temperature results in partial evaporation and decomposition of the nitric acid. High temperature is particularly dangerous when spent acid, containing ~~XXXX~~ nitro product, is employed.

The simplest method of mixture is that employing the bubbling of air through the

73

acid (Fig.14). However, it is used only in rare cases, as the bubblers undergo extraordinary corrosion and ~~the~~ become clogged with deposits of mineral ~~acid~~ salts. Moreover, HNO_3 and SO_3 is expelled from the mixed acid, and it undergoes dilution by the moisture of the air.

A more widely used method of mixing of acids is that employing a circulation pump (Fig.15), which permits the mixture to be driven through a condenser at the same time.

Upon completion of the ~~mixing~~ mixing, the ready mixture is forced out of the mixer, when the first approach is used, by ~~compressed~~ compressed air, through the condenser into ~~the~~ storage, whereas under the second approach, delivery of the mixture into storage is performed by the same pump.

74

Mechanical mixture of acids if a proper cooling surface is present within the mixer (for example, a coil or jacket) is a higher-output method, and requires less space (Fig.16), and therefore it is employed at all plants where ready-made mixed

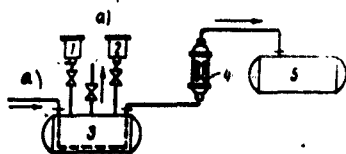


Fig.14 - Compressed Air Mixing of Acids

1, 2 - Metering devices; 3 - Mixture;
4 - Condenser; 5 - Storage

a) Compressed air

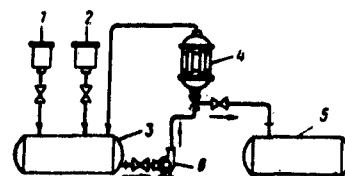


Fig.15 - Circulation Mixing of Acids

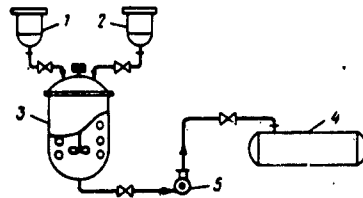
1, 2 - Metering devices; 3 - Mixer;
4 - Condenser; 5 - Storage; 6 - Pump

acids are used. The mixing speed is determined almost entirely by the heat-engineering data for the apparatus, and therefore, a speeding of the cooling process in the mixture makes it possible to increase the output capacity of the equipment.

The mixer has to be provided with a local type of ventilating device, because a gas phase containing nitrogen oxides is present above the nitro mixture.

Because of the aggressiveness of the acids, the sequence in which the components are charged into the mixture is of major significance in batchwise mixing. If the mixer is of a standard steel, the acids must be charged in the following sequence:

- 1) ~~XXXXXX~~ strong sulfuric acid (oleum or commercial sulfuric acid);
 - 2) nitric acid;
 - 3) water.
- The mixer is of chrome-nickel steel, the sequence with which the components are charged is changed to: 1) nitric acid; 2) strong sulfuric ~~XXX~~ acid; 3) water.



Mixing
Fig. 16 - Mechanical ~~XXXXXXXX~~ of Acids
1, 2 - Metering devices; 3 - Mixer;
4 - Storage; 5 - Pump

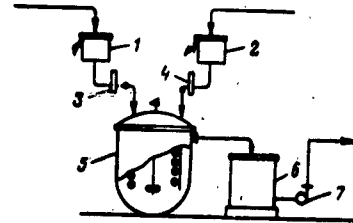


Fig. 17 - Continuous Mixing of Acids
1, 2 - Pressure tanks; 3, 4 - Metering
devices; 5 - Mixer; 6 - Receiving tank;
7 - Pump

Batchwise mixing of acids usually ^{is} employed only where the mixed acid must be accurate to very high precision, and consumption is comparatively low. Whereas ~~XX~~ achievement of high accuracy in mixture composition is a positive quality of this arrangement, the

bulkiness of the equipment often compels this to be abandoned, and continuous mixing to be substituted therefore.

Continuous mixing of acids is performed in accordance with the diagram illustrated in Fig. 17, wherein we see that components coming from pressure tanks IX are delivered continually into the mixer by gravity, via metering devices. The finished mixture flows into the receiving tank and is then pumped continually into storage by a centrifugal pump. The output rate of ~~such~~ equipment for continuous mixing is increasing very rapidly, and is limited only by the removal of the heat IX emitted upon mixing. The temperature in the mixture ~~IX~~ is usually held to not over 50°C, for the reasons

indicated above. The charging of the components is virtually simultaneous, in continuous mixing, but when the unit is started it is necessary, if corrosion is to be avoided, to use the same sequence of charging as in batchwise mixing.

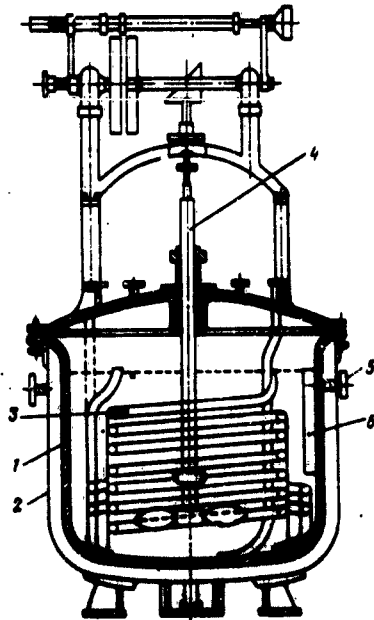


Fig. 18 - Mixture

1 - Shell; 2 - Jacket; 3 - Coil;
4 - Impeller shaft; 5 - Drainage
flange; 6 - Drainage trap

A principal piece of equipment used consists of a mixer and metering device. The simplest design of continuous mixer is that illustrated in Fig. 18: The apparatus consists of a cylindrical vessel with a spherical top and bottom. The upper portion of the cylinder contains a drainage flange for emission of the finished mixture, whereas, within the cylinder, and opposite this flange, is a drainage trap, making

it possible to remove the nitro mixture from the lower portion of the apparatus. The components to be mixed are delivered to the ~~upper~~ upper portion of the apparatus. The location of the coil, the passage of the agitator through the top of the apparatus, the thermometer and other details are analogous to details found in batch-type nitrators. Continuous metering of the components can be performed through metering devices of various designs: variable-area flow meters, ~~plunger~~ ^{plunger} and membrane pumps, etc., for liquids; and hoppers with belt or worm conveyors, in the case of solid substances.

E. ~~XXX~~ Reworking the Spent Acids

Section 1. Denitration of Spent Acids

The function of the denitration shop is to process the spent acid so as to extract the nitric oxides and nitric acid converted into weak nitric acid by means of an absorption system. Further processing of the denitrated sulfuric acid thus obtained in the concentration shop makes it possible to produce an acid ~~XXI~~ suited for recycling for nitration. Thus, a denitration installation, combined with a concentration installation, makes it possible to set up the closed cycle of utilization of sulfuric acid, as a nitration medium, and to return for nitration in the form of weak nitric acid, the nitric oxides and nitric acid in the initial spent acid.

Special requirements have to be met by the spent acid if the denitration process is to be performed successfully and without danger. They pertain to the level of nitro product content therein, and the strength of the sulfuric acid. The presence of nitro products in the spent acid is undesirable, ~~XX~~ inasmuch as they are driven off into the denitration column and, entering the apparatus of the absorption system, contaminates

the nitric acid produced with products of resinification.

The acid to be denitrated must not contain more than 1% nitro products. Moreover, the presence of any nitro product is permissible only in the form of the mononitro derivative. The presence of polynitro derivatives may make the process subject to explosion. However, mononitro derivatives may also undergo nitration, to di-, and, particularly to the highly explosive trinitro derivatives in the process of denitration, and this must always be borne in mind. The spent acid is subjected to long-term settling before it goes to denitration, in order to extract ~~XXXX~~ the nitro products to the maximum degree.

Spent acids containing polynitro derivatives as impurities (resulting from the production of TNT and picric acid), must undergo special cleansing to avoid precipitation of the volatilized nitro products in the upper portions of the condenser, and the explosion that may result as a consequence. Usually, polynitro compounds are extracted from ~~XX~~ these spent acids by means of organic solvents.

As already indicated, denitration is a process of ~~XXXXXX~~ extracting residual nitric acid and nitrogen oxides combined in nitrosyl sulfuric acid HNSO_3 , from the mass of dilute sulfuric acid. Nitrosyl sulfuric acid is itself ^{an} ~~XX~~ unstable compound, the crystals of which rapidly decompose upon heating. However, solutions of nitrosyl sulfuric acid in sulfuric acid at 75% H_2SO_4 and higher strengths are very stable. When the strength of the sulfuric acid is reduced to 70%, ~~XXXXXXXXXXXX~~ ^{decomposition} of the nitrosyl sulfuric acid proceeds quite rapidly. Increase in the rapidity of decomposition is also facilitated by increasing the temperature and by the presence of nitric acid. This latter is explained by the following reaction:



However, the concentration of sulfuric acid in the spent acid is the chief factor determining the denitration process rate. With increase in concentration, the rate diminishes, and vice versa. The optimum concentration of spent acid is 70 - 72% H_2SO_4 . At lower concentrations, an exceedingly weak denitrated acid is obtained, whereas increase in strength to over 72% H_2SO_4 reduces the output capacity of the denitration column.

Thus, complete separation of nitric acid and nitrogen oxides from mixture with sulfuric acid requires dilution of the latter to 70%, followed by heating to a temperature that makes for complete driving off of the volatiles. The nitric acid vapors resulting concentrate into liquid in which the nitrogen oxides are absorbed. Final oxidation of the nitrogen oxides to ~~HN~~ nitric acid occurs as a consequence of mixing with the oxygen of the air.

The process of denitration of the spent acid is most ~~HN~~ simply performed in a denitration column provided with condensers for cooling the nitrous gases, and with an absorption column for absorbing them, with subsequent conversion to nitric acid.

Figure 19 depicts the ^{schematic} design of a denitration system consisting of a denitration column, a condenser from which the nitro product~~y~~ with the weak nitric acid flows into a separator, where it undergoes separation, and the nitric acid flows into a receiver from which a centrifugal pump delivers ^{it} to concentration. The spent acid is delivered from the settling column to a pressure metering tank, from which it flows to the column into which live steam is delivered through a tube. The denitrated acid flows from the column through ~~XXXXXX~~ an hydraulic seal into a receiver from which it is delivered to concentration by a centrifugal pump. The acid receivers are equipped

with coils into which water is delivered for cooling.

The denitration column is made of acid-resistant material with packing. The column is made of steel lined with acid-resistant plates. In recent years, columns consisting of 12 - 14 individual rings of silicon thermosilid mounted on a foundation of acid-resistant cast iron, have come into use. Between the rings, plates with central openings are fastened; they have flanges covered by a hood with apertures left for the passage of gas. At the top, the column is covered by a hemispherical cover with the flange for removal of nitrous gases.

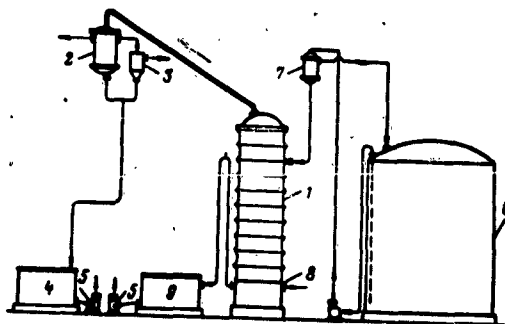


Fig.19 - Diagram of Denitration System

1 - Denitration column; 2 - Condenser; 3 - Separator; 4 - Nitric acid receiver; 5 - Pumps; 6 - Settling column; 7 - Metering tank; 8 - Nozzle for introduction of live steam; 9 - Sulfuric acid receiver

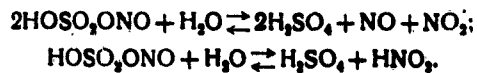
The spent acid is sent into the upper portion of the column through a distributor in the form of a stream HX that irrigates the packing, passes through the slit between hood and plates, and drips downward countercurrent to saturated HX or overheated steam (250°C) delivered into the lower portion of the column.

The chemistry of the denitration process may be explained as follows. The spent

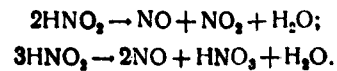
acid entering the column is heated, and the nitric acid it contains undergoes complete decomposition in accordance with the following equation



The remaining nitrosyl sulfuric acid decomposes ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXX~~ under the influence of the steam, as it passes through the column, in accordance with the equations:



The nitrous acid that is formed decomposes further, because of its instability, in accordance with the following equations:



The nitric acid and nitric oxides ~~IX~~ obtained as a consequence of the decomposition, as well as the nitro products dissolved in the spent acid, are driven off from the column into a condenser by 'live' steam. The nitro product nitric acid and steam condense in the condenser, and the residual gases go into the absorption column. The denitrated spent acid, containing 67 - 70% H_2SO_4 , ~~IX~~ emerges from the lower portion of the column through an hydraulic seal into a cool collector. The products of the denitration apparatus, weak nitric and weak sulfuric acid, then go to concentration.

78

Section 2. Concentration of the Denitrated Acids

The sulfuric acid obtained after denitration is concentrated by flue gas. The process occurs by blowing the gas through two or three chambers in direct or countercurrent motion, with the ~~IX~~ aid of bubbling tubes, through a system consisting of strong acid and hot flue gases. The flue gases, at 650 - 1000° temperature, are produced in a free-standing furnace by burning residual oil.

The denitrated acid coming from the furnace for concentration has to contain not less than 65% H_2SO_4 , not more than 0.05% N_2O_3 , and not more than 0.5% nitro product.

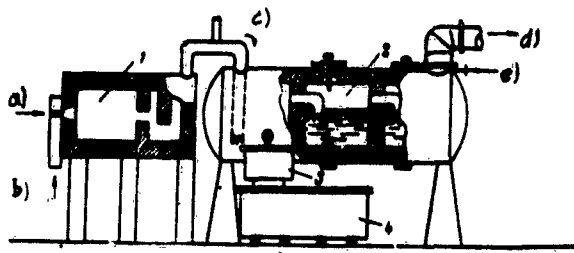


Fig.20 - Unit for Concentration of Sulfuric Acid

1 - Furnace; 2 - Concentrator; 3 - Condenser; 4 - Collector for steamed acid

a) Fuel; b) Air; c) Flue gases; d) To electrical filter;
d) Denitrated acid

The drum-type concentration assembly (Fig.20) consists of a furnace, concentrator, and an electrical filter to trap the sulfuric acid fumes, a collector for the acid being vaporized, a condenser, and a collector for the vaporized acid. The furnace and the concentrator are on high foundations to permit the acid to flow from the apparatus to the condenser by gravity, and then to flow into the commercial sulfuric acid collector.

The furnace consists of refractory brickwork in a steel jacket lined with sheet asbestos. It is separated, by a grillwork barrier, from the chamber for combustion of the fuel and mixing of the heated gases with the reheated air. The air required for heating, as well as the reheat air, are forced into the furnace under pressure which assures bubbling of the heated gases through the layer of acid in the concentrator chambers.

78

The concentrator is a horizontal welded cylinder of boiler iron lined with two layers of asbestos board, and the asbestos is lined in turn with sheet lead and lined andesite rock over andesite putty. The drum is internally divided by partitions into two ~~chambers~~ or three chambers, depending upon the strength of the commercial sulfuric acids to be taken from this installation. The two-chamber concentrator will provide sulfuric acid at 92 - 93% H_2SO_4 , whereas the three-chamber will yield 95 - 96% H_2SO_4 . The three-chamber-type ~~concentrator~~ has a larger furnace and three bubbling tubes instead of two, as one finds in the two-chamber concentrator.

79

The concentrator has an electrical filter, lined with andesite and provided with graphite carbon or thermosilid plates; a corona-discharge electrode is ~~used~~ suspended in each tube. The gases obtained upon the burning of liquid or gaseous fuel in the furnace, have a temperature of 650 - 1000°, enter the first chamber of the concentrator under pressure, then go to the second, and third, from which they proceed to the electrical filter and then into the atmosphere.

The denitrated hot acid proceeds continuously by gravity through an acid line from the denitration column to a pressure tank and then, again by gravity flow, moves along with the acid ~~which~~ deposited in the electrical filter to a concentrator from which, moving countercurrent to the heated gases, it passes through the vaporization chamber and enters the condenser in the hot state (at a temperature of 220 - 250°). The commercial sulfuric acid leaves the condenser at a temperature of 45°C, and flows into a collector.

The commercial sulfuric acid obtained as a consequence of denitration and concentration is either reused to make nitrating ~~mixtures~~ mixtures, or goes to produce oleum.

F. Absorption of the Nitric Oxides

One of the important elements in the acid department of an explosives plant consists of absorption installations for absorbing nitric oxides liberated upon the denitration of the spent acids, and from the nitration apparatus. Absorption of nitric oxides has two purposes: removing harmful elements from work areas, and eliminating losses of valuable products (NO , NO_2 , HNO_3).

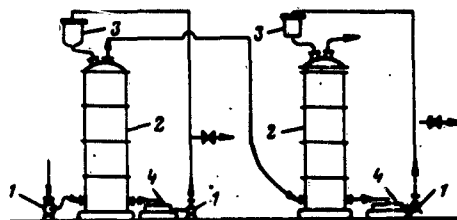


Fig.21 - Two-Tower ~~XXXXXX~~ Nitric Oxides Absorption Unit

1 - Pump; 2 - Absorption column; 3 - Pressure Tower;

4 - Receivers

~~XXXX~~ Satisfactory absorption of nitric oxides is achieved if there are two absorption towers as shown in Fig.21. An increase in the number of towers makes ~~XX~~ for more complete absorption of the nitric oxides.

The mixture of gases containing nitric oxides is driven, by fan, into the absorption column filled with Raschig rings and irrigated with water, which enters the column from a metering pressure tank or water main. Oxidation of NO to NO_2 occurs in the first column. The nitric acid converted in this column flows into a collector and is delivered from there by pump to the acid department. The gases emitted from the first column are directed to the second column for reabsorption. This column has

~~XXXXXX~~

79

the same setup as the first, in which the reflux of the sulfuric acid coming from the pressure tank occurs. The nitrosyl sulfuric acid formed in this column flows into the receiver, from which it is pumped back to the denitration department, and partially into the pressure tank.

80

Figure 22 shows another design of three-column absorption setup. The first column undergoes weak nitric acid ~~reflux~~ reflux, the second has water reflux, and the third - lime water from pressure tank.

The nitration departments also have absorption installations of this kind, as considerable quantities of nitric oxides, nitric acid vapor, and in some cases, even vapors of the nitro products are liberated from the nitrators in operation. The gases are picked up from this apparatus into a gas line, and channeled to the absorption stations. To trap the nitric acid and nitro product vapors, the gases are passed

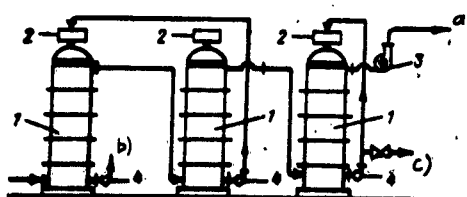


Fig.22 - Diagram of Three-Column Installation for Absorption of Nitric Oxides

1 - Absorption columns; 2 - Pressure tanks; 3 - Fan; 4 - Pump

a) To atmosphere; b) To HNO_3 collector; c) To waste drainage

into
through a special condenser, from which condensate flows ~~into~~ into a special tank, from which it is driven into the weak nitric acid storage.

CHEMISTRY AND TECHNOLOGY OF NITRO COMPOUNDS OF
AROMATIC SERIES

A. TNT and Other Nitro Derivatives of Toluene

TNT is obtained by the nitration of toluene. Six isomers of TNT are known², having the same general formula $C_6H_2(NO_2)_3CH_3$, ^{but} differing by the difference in the positions of the nitro groups in the benzene ~~XXXXXXXX~~ ring, and therefore having different physical-chemical properties. The TNT that has practical utilization consists primarily of symmetrical or ~~XX~~ α -isomer ~~XXXXXXXXXXXX~~ trinitrotoluene.

TNT was first produced in 1863 (Bibl.1), and introduced into munitions use at the beginning of the Twentieth Century. It ~~XXXXXXXX~~ became the most important explosive as early as World War I. Its production achieved particularly large scale during World War II, as is ~~XXXXXXXX~~ evident from data in Table II. The capacity of some plants making TNT reached 40,000 tons per year.

World War II,
During ~~XXXXXXXXXXXXXXXXXXXX~~ TNT was the major high explosive. Whereas, during World War I, other nitro derivatives ~~XXXX~~ of aromatic compounds were employed in considerable quantities in addition to TNT, during ~~XXX~~ World War II, TNT or mixtures based thereon (ammotols, alloys of TNT and RDX, etc.) had the field entirely to themselves. Thus, for example, the mean monthly output of the German war plants

²If we disregard nitrotoluenes containing the NO_2 group in the side chain, for example, *ortho*-nitrophenylidinitromethane, obtained by Wilson in 1946 (Bibl.2).

was (in tons):

TNT	21,000
Picric acid	850
RDX	700
Ammonium nitrate	18,000

Table 11

a)	b)		
	1905	1918	c)
d)	118	49 860	189 131 (1943)
e)	—	60 000	180 000 (1939)
f)	—	—	more 1 000 000 (1945)

a) Country; b) Annual TNT output in tons; c) Second World War; d) Germany; e) England; f) USA

TNT is also widely employed to produce industrial explosives, the demand for which attains hundreds of thousands of tons per year.

The chief advantage of TNT is the fact that, although it is a bright explosive of rather high power, it is comparatively insensitive to mechanical effects, which makes possible its use in the loading of all kinds of munitions, including armor-piercing shells. A large source of supply for TNT production is available.

Thanks to its high chemical stability, the chemical and explosive properties of TNT are retained even upon long years (decades) of storage. However, its limited reactivity makes it possible to use it in the manufacture of a number of other explosives, for example, various mixtures and alloys with RDX, and mixture with ammonium nitrate. This improves the supply of explosives, which is an exceedingly important factor in war time.

Section 1. The Chemistry of Production, the Properties, and the Applications of Toluene and the Intermediates Produced in the Course of the Synthesis Thereof

The starting materials for the manufacture of TMT are: toluene, ^{nitric} ~~nitric~~ and sulfuric acids. Pure toluene $C_6H_5-CH_3$ is a colorless, highly refractive, transparent liquid. Its melting point is -95° (Bibl.3), its boiling point 110.6° , specific gravity $d_{40}^{20} = 0.867$. Toluene ignites readily and burns with a smoky flame. It is an excellent solvent for organic substances, and is itself readily soluble in alcohol, ether, and other solvents. Chemically speaking, toluene is a highly reactive substance. The hydrogen atoms in the benzene ring ~~XXXXXXXXXX~~ ^{one} of toluene are readily replaced by various groups or atoms (NO_2 , SO_3H , OH , J , Cl , etc.). Under the effect of oxidisers, the side chain ~~XX~~ oxidizes through the carboxyl group, and the ~~XX~~ toluene converts to benzoic acid.

Coal and petroleum are natural sources of toluene. Toluene is obtained from coal by treatment with coal tar, dry distillation products, and trapping of ^{coke-oven} ~~XXXXXXXXXX~~ gases. Toluene ~~XXXXXXXXXX~~ is derived from petroleum either in direct distillation or, most frequently, with the purpose of enriching the first fractions of petroleum with aromatic hydrocarbons. These, the kerosene fraction, are first ^{subjected} ~~XXXXXXXXXX~~ to pyrolysis.

Toluene is also obtained by catalytic aromatisation of naphthene and paraffin hydrocarbons in petroleum. This process was widely used in the United States during World War II, and in other countries in subsequent years. The separation and final cleansing employed therein include azeotropic distillation, extractive distillation, extraction by solvents, and cleaning by heat.

As a consequence of the relatively low content of toluene in natural sources,

manufacture by synthesis is necessary. Synthetic toluene is produced in a number of ways:

- 1) from benzene and methanol (an industrial method widely employed in Germany);
- 2) from benzene and dichloroethane in the presence of aluminum ~~chloride~~ ^{chloride,} with subsequent hydration by diphenylethane in the presence of nickel;
- 3) from benzene and methylchloride, also in the presence of aluminum chloride.

In view of the low boiling point of methylchloride (2°C), the substitution reaction has to be performed under pressure. This complicates the process and is a shortcoming of the method.

Synthetic toluene derived from benzene and dichloroethane is contaminated by resins and diphenylethane, and when obtained from benzene and methylchloride, it is contaminated by xylenes. Toluene obtained from natural sources is also not a chemically pure product. Toluene from coal contains paraffin and olefin hydrocarbons, whose boiling point approximates that of toluene. Impurities may run to 4 or 5%. Aside from paraffins, toluene contains approximately 1 - 1.5% of benzene, 0.5 - 1% xylene, and insignificant quantities of phenols and pyridine bases. In petroleum and pyrogenetic toluene, not ~~subjected to~~ ^{subjected to} special cleansing, there are gasolines, sometimes attaining 10 - 15% of the whole.

Nitration of contaminated toluene yields a ~~contaminated~~ contaminated nitro compound and also results in elevated consumption of nitric acid in the oxidation of certain of the impurities (paraffins, phenols) (Bibl.4). However, it is held, in Germany and England, that the separation of impurities of this type is more profitably performed after the toluene has been converted to mononitro compounds. Inasmuch as the boiling

point of the latter is more than 100° higher than the boiling point of impurities, it is considerably easier to drive them off (Bibl.5).

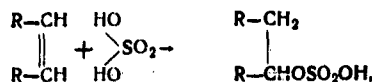
The most undesirable impurities are benzene and especially xylene. A 1% admixture of benzene in toluene reduces the freezing point of the raw TNT obtained by 0.35° , whereas the presence of 1% xylene reduces it by 1 - 1.2° . Gasolines also constitute harmful admixtures in toluene. They oxidize in the process of nitration. In addition to the consumption of nitric acid this gives rise to, it results in dilution of the mixture undergoing nitration by the water emitted in the course of oxidation. Each 1% of gasolines in the toluene requires approximately an additional ~~XXX~~ 25 kg of nitric acid per ~~XXX~~ ton of TNT. The unsaturated hydrocarbons accompanying the toluene also oxidize in the process of nitration. The consumption of nitric acid upon the oxidation thereof ~~is~~, when computed for 0.1 gm bromine number of toluene, comes to 6 kg per ~~ton~~ of TNT, or 0.5% by weight of the entire amount of nitric acid expended upon nitration.

Thus, the composition of the toluene has a significant effect upon the quality of the TNT, raw ~~material~~ ^{material} consumption, and the yield capacity of the apparatus. Therefore, the impurities content of ~~XXX~~ toluene used for nitration is held to specific limits. Thus, toluene from coal is required to be a colorless ~~XXXX~~ transparent liquid of specific gravity 0.865 ± 0.003 at 15°C , distilling at temperature within the range of $109.0 - 111.0^{\circ}$, corresponding to a content of not more than 1% benzene and 0.3% xylene. Toluene from oil should have a specific gravity of 0.865 ± 0.003 at 15°C , and should go over in the range of $109.0 - 111.25^{\circ}$, corresponding to no more than 2.2% gasolines therein; (xylene is not found in toluene from oil). ~~The broader boiling point range~~

63 in petroleum teluene is due to the fact that a greater quantity of impurities is permissible. This, it is understood, renders nitration and the production of quality TNT more difficult.

The unsaturated hydrocarbons content of teluene is determined by titration with bromine. The bromine titer showing the number of grams of bromine needed to take up the unsaturated hydrocarbons in 100 cc of teluene should not exceed 0.8 gm for coal teluene, or 0.4 gm for petroleum teluene.

The quantity of unsaturated hydrocarbons is also determined by testing with sulfuric acid. Sulfuric acid reacts with the unsaturated hydrocarbons, ^{attaching} ~~attaching~~ to them at the double bond, with the formation of ~~XXX~~ esters:



as well as polymerization and condensation products, dark in color. By comparing the intensity of the coloration of teluene mixed with an equal volume of commercial sulfuric acid, and a standard sample, one determines the relative content of olefins.

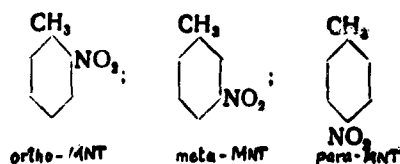
The temperature at which the teluene fraction begins to boil is affected by benzene, whereas the temperature at which boiling terminates is affected by xylene, unsaturated hydrocarbons, and gasoline. In the case of coal teluene, the temperature of the end of boiling (indicating the presence of xylene) is the more important characteristic, whereas for pyrogenetic teluene, from which xylene is lacking, the temperature of the onset of boiling is more important.

In nitration of teluene, the various isomers of mono-, di-, and trinitrotoluene form in sequence in various ratios.

Mononitrotoluenes are obtained by nitration of toluene with nitric acid or nitrous acid, on the equation



The result of this reaction is the formation of a mixture of three mononitrotoluene isomers: ortho, meta, and para



Mononitrotoluene XIX was first produced in 1838 (Bibl.6) by the action of nitric acid upon toluene. In 1841 (Bibl.7), mononitrotoluene was again obtained, and on this occasion its boiling point (225°C), and its specific gravity at 16°C, 1.18, was determined.

The properties of various mononitrotoluene isomers (Bibl.8) are illustrated in Table 12.

Table 12

Mononitrotoluene Isomers	Freezing Point °C	Boiling Point at 760 mm Hg °C	Specific Gravity d_{40}^{20}	Color and State at Room Temperature
Ortho-	-9.27, modification α , metastable -3.17, modification β , stable	221.7	1.163	Oily liquid, straw-yellow color
Para-	51.6	238.5	1.120 (at 54°)	Colorless crystals of rhombic system
Meta	16.1	232.7	1.168	Light yellow liquid

83

Technical mononitrotoluene is a liquid ranging from bright yellow to brown-red color depending upon the impurities. The color of mononitrotoluene is explained by

84

the presence of nitrocresols (Bibl.8). ~~3,5-dinitro-ortho-cresol and 3,5-dinitro-ortho-~~
 3,5-dinitro-para-cresol and 3,5-dinitro-ortho-cresol (Bibl.8 and 9) have been found in technical ~~XXXX~~ mononitrotoluene. Its specific gravity varies with temperature and is 1.162, 1.143, and 1.125 at 20, 40, and 60°C respectively.

The approximate percentage composition of mononitrotoluene obtained by nitration of toluene with mixed acid, and dependent upon temperature of nitration, is presented in Table 13 (Bibl.8, 10, 11):

Table 13

a)	b)				
	60	30-50	20	0	-30
c)	35,3	36,1	36,5-37,3	38,1	39,3
d)	59,6	59,2	59,4-59,5	58,0	57,2
e)	5,1	4,7	4,1-4,2	3,9	3,5

a) Mononitrotoluene isomer; b) Nitration temperature °C; c) Para-; ~~XXXX~~
 d) Ortho-; e) Meta-

The ~~XXXX~~ nitration temperature influences the quantitative relationship among the ~~XXXX~~ mononitrotoluene isomers formed. When it is increased, the quantity of meta- and ortho-isomers increases somewhat, and the quantity of the para-isomer diminishes (Bibl.12).

Despite the substantial para-isomer content, this isomer having a freezing point of 51.6°C, technical mononitrotoluene is a liquid that freezes completely at -16°C, although the para-isomer begins to freeze at about 0°C. This property is employed

84 in technology for the separation of the mononitrotoluenes: the para-isomer freezes first, whereupon the ortho-isomer is driven off the meta-isomer under vacuum, making use of the comparatively greater difference in the boiling points of these two (see

Table 14

a)	b)	
	20°	50°
50	0,04	0,08
75	0,50	0,81
80	1,56	2,09
85	2,73	12,28
88	19,5	20,14
90	32,2	33,90

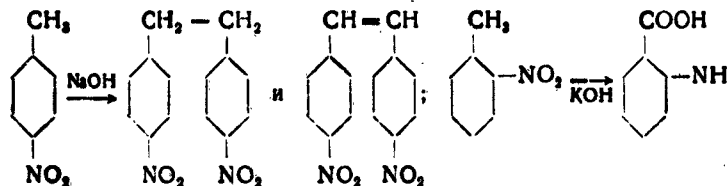
a) Strength of H₂SO₄, %; b) Solubility in percentage (weight) at the following temperatures

Bibl.13 for a potentiometric method of determining meta-nitrotoluene in a mixture thereof with ortho-nitrotoluene).

Mononitrotoluene is virtually insoluble in water, but readily soluble in organic solvents.

The solubility of technical mononitrotoluene in sulfuric acid is presented in Table 14.

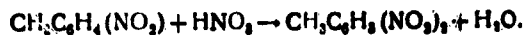
Mononitrotoluene is highly reactive (Bibl.14 presents the mechanism of activation of the methyl group in nitrotoluenes). Its para- and ortho-isomers react even with weak caustics in accordance with the equations



85 This reaction does not proceed with the meta-isomer.

Mononitrotoluene is not an explosive. It is used, to some extent, as a phlegmatizer of explosives of high sensitivity. A substantial amount of mononitrotoluene is employed in the production of teluidine, which is used in the

Dinitrotoluene is ~~not~~ obtained upon the nitration of mononitrotoluene by mixed acid in accordance with the equation

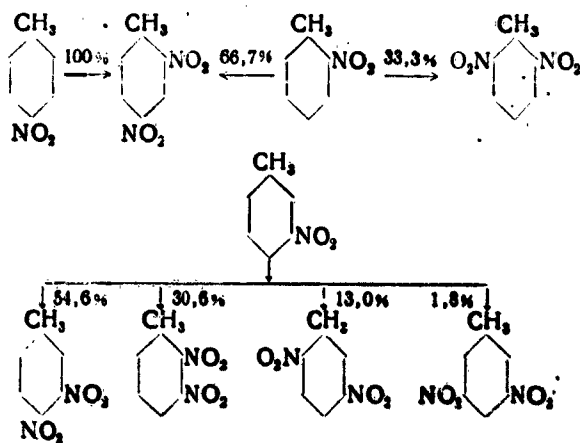


Nitration of technical ~~mononitrotoluene~~ mononitrotoluene, which is a mixture of three isomers, yields technical dinitrotoluene, consisting of a mixture of six isomers.

According to De Beule (Bibl.8) the ~~approximate~~ percentage composition of technical dinitrotoluene is:

2,4-dinitrotoluene	75.6
2,6-dinitrotoluene	19.7
3,4-dinitrotoluene	2.57
2,3-dinitrotoluene	1.44
3,6-dinitrotoluene	0.61
3,5-dinitrotoluene	0.68

Upon nitration of each of the isomers of mononitrotoluene, the following quantities of isomers ~~of~~ dinitrotoluene are obtained (Bibl.8, 11, 15, 16, 17, 18 19):



The physical properties of the isomers of dinitrotoluene are illustrated in

Table 15 (Bibl.8, 20).

Table 15

a)	b)	c)
2,4-	69,95	d)
2,6-	65,1	
3,4-	58,5	
2,3-	59,23	
3,6 (2,5)-	50,25	
3,5-	92,1	

a) Dinitrotoluene isomers; b) Freezing point, °C; c) Boiling point, °C;

d) Boils with decomposition at 300°C and normal pressure

Technical dinitrotoluene, consisting chiefly of 2,4-isomer, consists of a crystalline substance, ~~yellow~~ yellow in color, with a freezing point of 50 - 54°, and considerable oily impurities. Its specific gravity at 71°C is 1.32; its specific heat is 0.33 kcal/kg/°C.

Technical dinitrotoluene dissolves better in organic solvents than does trinitrotoluene, but its solubility in water is negligible.

The solubility of technical dinitrotoluene in sulfuric acids of various strengths is presented in Table 16.

It may be seen ~~in~~ (Bibl.21) for freezing points of alloys of 2,4-dinitrotoluene with para-monomitrotoluene; (Bibl.22) provides the refractive indices of alloys of para-monomitrotoluene, 2,4-dinitrotoluene, and 2,4-trinitrotoluene. A diagram ~~of~~ of ~~the~~ the feasibility of mixtures of 2,4-dinitrotoluene with 1-, 3-, and 5-trinitrotoluene is shown in (Bibl.23).

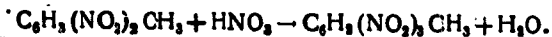
Table 16

a)	b)							
	20	40	50	60	70	80	100	120
80.0	1,2	—	2,5	—	3,8	—	—	—
83,6	—	3,6	4,7	5,6	6,3	6,4	6,4	8,5
88,7	6,1	10,0	12,8	18,3	—	—	—	17,4
90,0	8,5	—	16,8	—	20,0	—	—	—
93,0	—	26,4	33,8	53,4	58,3	59,3	62,4	66,6
99,8	—	72,6	144	337	1121	1191	1360	—

a) Strength of H₂SO₄ in %; b) Solubility of dinitrotoluene (in 100 gm acid) in gm, at ~~XXXXXXXX~~ indicated temperatures in °C

Unlike mononitrotoluene, dinitrotoluene is an explosive, but a comparatively weak one. In the crystalline form, with cap No.8, it produces a 210 cc expansion in a lead bomb, but in view of its poor sensitivity to detonation, it is ~~IX~~ not employed ~~XXXXXXXXXX~~ by itself as an explosive. A small quantity thereof is employed in the fabrication of nitroglycerin powder, ~~XXXXXX~~ where it is used as a plasticizer.

TNT is obtained by the nitration of dinitrotoluene with mixed acid, according to the scheme



Nitration of technical dinitrotoluene which consists of six isomers yields technical TNT, also consisting of six isomers, the approximate quantitative relationship among which is shown in Table 17.

87 Not infrequently, TNT also contains some amount of 2,4- and 2,6-dinitrotoluene [by the results of colorimetric determination of the isomers of dinitro~~XX~~ and trinitrotoluene (Bibl.8)].

The nitration of each of the isomers of dinitrotoluene yields the following quantity of isomers of trinitrotoluene (Bibl.8):

Table 17

a)	b)	
	30°	50°
c)	95.50	95.10
d)	1.25	1.35
e)	2.47	2.69
f)	0.27	0.29
g)	0.009	0.009
h)	0.002	0.002
i)	0.30	0.33
j)	0.13	0.15
k)	0.06	0.06

a) **XXI** Components; b) Composition of technical TNT in accordance with nitration temperature of toluene to mononitrotoluene, %; c) α (2,4,6)-trinitrotoluene;

d) β (2,3,4)-trinitrotoluene; e) γ (3,4,6 and 2,4,5)-trinitrotoluene;

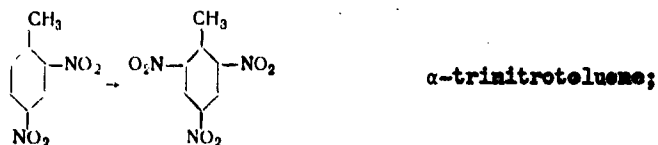
f) η (2,3,6 and 2,5,6)-trinitrotoluene; g) ϵ (2,3,5)-trinitrotoluene;

h) δ (3,4,5)-trinitrotoluene; i) 2,3-dinitrotoluene; j) (3,6 and 2,5)-dinitrotoluene;

k) 3,5-dinitrotoluene

87

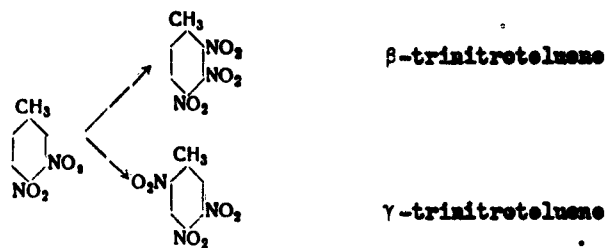
a) nitration of 2,4-dinitrotoluene **XXII** yields only symmetrical α -trinitrotoluene with 80, 85°C **XXI** as the freezing point of the chemically pure product (Bibl.1, 8, 24):



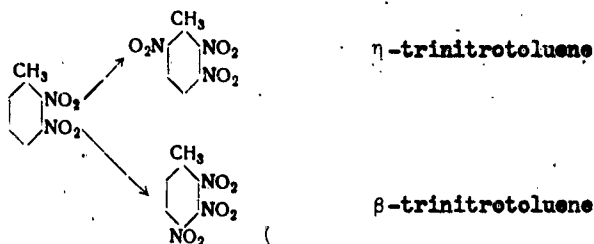
b) nitration of 2,6-dinitrotoluene also yields **XXI** only α -trinitrotoluene (Bibl.6).



c) nitration of 3,4-dinitrotoluene yields two isomers γ -2, 4, 5-(3,4,6)-trinitrotoluene (84%) (Bibl.25) and β -2, 3, 4-trinitrotoluene (16%) (Bibl.8, 24):

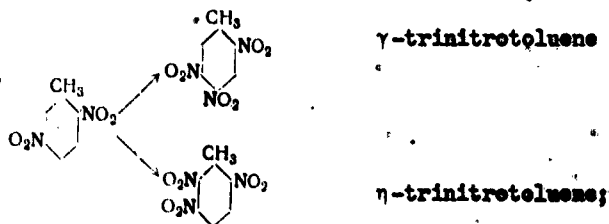


d) nitration of 2,3-dinitrotoluene also yields two isomers β -(2,3,4)-trinitrotoluene (62.2%) and η -(2,3,6- or 2,5,6-)-trinitrotoluene (15.5%) (Bibl.26), and 22.3% 2,3-dinitrotoluene remains unreacted (Bibl.8)

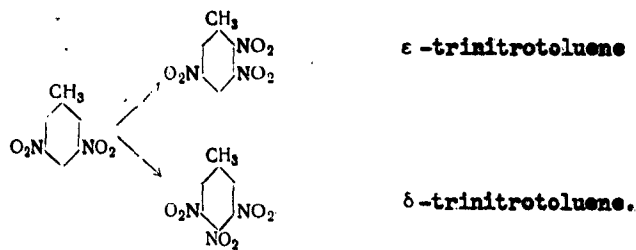


2,3-dinitrotoluene nitrates with considerably greater difficulty than 2,4-, 2,6-, and 3,4-dinitrotoluene;

e) dinitrotoluene 2,5-(3,6-), like the 2,3-isomer, also nitrates with difficulty, and yields 66.7 - 69.7% γ -(3,4,6- or 2,4,5-)-trinitrotoluene, 8.2 - 8.6% η -(2,3,6- or 2,5,6-)-trinitrotoluene and 21.7 - 25.1% remains ~~XXXXXXXXXX~~ unnitrated 2,5-dinitrotoluene (Bibl.8):



f) nitration of 3,5-dinitrotoluene under ordinary circumstances leads to partial destruction (Bibl.8, 26). However, the main bulk of the 3,5-dinitrotoluene remains unchanged. When it is nitrated with mixed acids stronger than the ordinary, nitration accompanied by oxidation occurs. The result is 73% unreacted 3,5-dinitrotoluene, 11% of 2,3,5- or ϵ -trinitrotoluene (Bibl.27), 2% of 3,4,5- or δ -trinitrotoluene (Bibl.28), and 14% is lost by oxidation (Bibl.8):



The freezing points of isomers of trinitrotoluene are illustrated in Table 18 (Bibl.8, 29).

Table 18

a)	b)
c)	102,3
d)	110,3
e)	109,8
f)	95,2
g)	132,0

a) Isomers; b) Freezing point, °C; c) ν (2,4,5 or 3,4,6)-trinitrotoluene; d) β (2,3,4)-trinitrotoluene; e) η (2,3,6)-trinitrotoluene; f) ϵ (2,3,5)-trinitrotoluene; g) δ (3,4,5)-trinitrotoluene

The specific gravity of all the isomers is approximately 1.62. The flash point is 290 - 310°. In the Transl block, they show identical expansion, and virtually identical sensitivity on the impact testing machine.

Technical TNT contains not only the nitro derivatives of toluene, but small amounts of oxidation and resinification products as well, plus nitration products of toluene impurities.

The oxidation products in TNT include substances of phenol character, constituting nitrocresols and derivatives of diphenyl or stilbene (Bibl.30). In the more powerful oxidizing processes involved in oxidation of the methyl group of the toluene, trinitrobenzoic acids are formed from the α - and other isomers of TNT. Symmetrical trinitrobenzoic acid yields CO_2 by cleavage rather easily when heated and undergoes conversion to trinitrobenzene. This occurs primarily when the TNT is washed with hot water. ~~As~~ Asymmetrical trinitrobenzoic acids undergo hydrolysis when boiled with water, to form dinitrooxybenzoic ~~XXXXXXXXXX~~ acids.

The quantity of oxidation products in spent acids of TNT manufacture rises from stage to stage and, in the third stage, constitutes about 5% of the weight of the raw TNT obtained. The oxidation products are, for the most part, nitrobenzoic acids, but a small amount of nitrocresols are also present.

Under severe processing conditions, (long periods of contact or high temperature of the order of 120°C), the TNT undergoes ~~III~~ high degree of oxidation by the nitro mixture when it is of the following composition: 84.05% H_2SO_4 and 16.65% HNO_3 (about 10% less in weight per hr). A ~~III~~ reduction in the nitric acid share of the mixed acids, and ~~IIII~~ reduction in temperature, will reduce the processes of oxidation. A 10° reduction in temperature (in the 85 - 115°C interval) cuts the intensity of the processes of oxidation virtually in half.

As a consequence of the oxidizing processes involving destruction of the benzene

ring, tetranitromethane, which gives TNT the odor of nitric oxides, is formed in the nitration dinitrotoluene.

It has been established (Bibl.31) that the nitration of technical dinitrotoluene accompanied is ~~accompanied~~ by oxidation with liberation of gaseous products consisting chiefly of carbon monoxide and carbon dioxide. It is held that this oxidation occurs ^{not} at the expense of the trinitrotoluene, but of the dinitrotoluene.

The major ~~impurities~~ impurities found in substantial quantities in TNT are isomers thereof and of dinitrotoluene. Inasmuch as the isomers of TNT, and those of dinitrotoluene as well, in part, are formed from metanitrotoluene, this last is the primary source of impurities in TNT. In point of fact, if the mononitrotoluene liberated from the meta-isomer is nitrated, it is possible to produce TNT at a freezing point of about 79° without further purification.

The asymmetrical trinitrotoluenes and other impurities present in raw TNT reduce the freezing point of TNT to 75 - 77°C, to form multi-component eutectic alloys of low melting point with α -trinitrotoluene. Some of these alloys are liquid at room temperature, ^{and} oily in appearance, and are therefore termed trotyl oil.

In storing munitions in which the filler is raw TNT, one observes a leakage of trotyl oil, resulting in a reduction of the density and strength of the explosive shell. This makes such munitions dangerous and of low quality (duds). In the case of artillery shells and mines, this may be the cause of premature explosions when fired. Incomplete explosions and duds are usually explained by the fact that the oily impurities, filling the space between the propellant and the explosive charge, ~~obstruct~~ obstruct the latter, and if they penetrate into the fuse, tend to impregnate the detonator and

may be explained by make it poorly sensitive to the cap. Premature explosions ~~XXXXXXXXXXXX~~ the fact that the leakage of oily impurities from shells destroys the monolithic nature of the explosive ~~XXX~~ charge, causing it to become porous, which may, when it is fired, result in dangerous intermixtures of explosive substance.

As a consequence of the causes indicated above, ^{impure} ~~XXXXXXXXXX~~ TNT should be employed only for the manufacture of explosive mixtures designed for early use, for example, for excavation by explosives. However, TNT to be employed to fill shells which is planned to store for a long period must under all circumstances be cleaned. Shells are filled with cleaned TNT, consisting of a virtually pure symmetrical 2,4,6- or α -isomer trinitrotoluene.

2,4,6- or α -trinitrotoluene is a white substance (growing yellow in the ^{light} ~~XXXXX~~) and having two polymorphic crystalline forms.

An x-ray study of 2,4,6-trinitrotoluene has shown that this compound may exist in either monoclinic and ortho-rhombic forms. The unit cell of the monoclinic form has the following dimensions: $a = 21.35 \pm 0.55$; $b = 0.05 \pm 0.03$; $c = 14.96 \pm 0.05 \text{ \AA}$ and $\beta = 111.15 \pm 15$, while the data for the ortho-rhombic form are $a = 20.7 \pm 0.68$; $b = 6.09 \pm 0.54$, $c = 15.03 \pm 0.07 \text{ \AA}$ (Bibl.32).

The freezing point of 2,4,6-trinitrotoluene is $80, 85^\circ$; specific ^{gravity} ~~XXXXXXXXXX~~ 1.663, while that of the ~~XXX~~ fused materials (at 82°C) is 1.467. The gravimetric density of ~~XXXX~~ crystalline trinitrotoluene is 0.9 - 1.0.

The density of compressed α -trinitrotoluene depends upon the pressure and ranges from 1.54 to 1.62 as pressure is varied from 1450 to 4350 kg/cm^2 . The density of a casting obtained upon ~~XXX~~ rapid cooling and agitation of fused α -trinitrotoluene fluctuates in the 1.55 - 1.60 range, while the addition of insignificant quantities of

other nitro compounds which prevent proper crystallization of α -trinitrotoluene makes for an increase in the density of the casting.

The density⁴ of solid and liquid trinitrotoluenes at various temperatures are presented in a work by Lewis (Bibl.33). For data on the rate of linear crystallization of trotyl, containing different amounts of dinitrotoluene or other aromatic nitro compounds, see elsewhere (Bibl. 34).

The latent heat of fusion of α -trinitrotoluene is 21.41 cal/gm, the heat of ~~the~~ crystallization is 5.6 kcal/mole (Bibl.29), and the heat conductivity at 25°C is 0.00055 cal/sec/cm³ °C. The vapor pressures of TNT at various temperatures is offered in(Bibl.35).

The hygroscopicity of ~~XXXXXX~~ α -trinitrotoluene is about 0.05%, and therefore it is not necessary to seal it airtight for storage.

The solubility of α -trinitrotoluene in water is low. Thus, at 15°C, 0.02 parts ~~XXXX~~ dissolve in 100 parts water, and at 100°C, 0.15 part α -trinitrotoluene dissolve in 100 parts water.

The low solubility of α -trinitrotoluene in water is a favorable property that makes it easy to use water to wash it free of acids. Nevertheless, this solubility results, on the one hand, in some loss of product, and on the other hand, in contamination ^{the} of water. Water containing 0.15% α -trinitrotoluene cannot be discharged into bodies of water, and therefore prior to discharge therein, it is subjected to cooling and allowed to settle, with the object of separating out the main mass of the dissolved TNT.

α -Trinitrotoluene dissolves quite well in~~the~~ organic solvents. Its best solvents are: pyridine, acetone, benzene, ~~XXX~~ toluene, and chloroform. α -Trinitrotoluene

dissolves poorly in ether and carbon disulfide. Table 19 (Bibl.36) shows the solubility of α -trinitrotoluene in various solvents.

Table 19

a)	b)									
	c)	d)	e)	f)	g)	h)	i)	j)	k)	l)
0	0,01	—	28	57	13	—	0,2	0,6	—	—
15	0,012	—	45	92	50	—	0,5	1,1	2,8	0,3
20	0,013	—	55	100	67	—	—	1,2	3,3	0,5
25	0,015	158	67	132	88	70	0,8	1,5	—	—
30	0,017	—	84	156	113	100	—	1,8	4,6	0,8
35	0,022	215	104	187	144	—	1,3	2,3	—	—
50	0,047	370	208	376	284	300	3,2	4,6	—	—
60	0,067	600	367	600	478	—	6,9	8,3	—	—
70	0,087	1250	826	1350	1024	—	17,3	15,1	—	—
75	0,087	2460	1685	2678	2028	—	24,3	19,5	—	—
100	0,147	—	—	—	—	—	—	—	—	—

a) Temperature, °C; b) Solubility of α -trinitrotoluene, in gm (in 100 gm of solvent);
 c) Water; d) Pyridine; e) Toluene; f) Acetone; g) Benzene; h) Dichloroethane;
 i) Carbontetrachloride; j) 95% ethyl alcohol; k) Ether; l) Carbon disulfide

91

The best solvent for purposes of crystallization is that which is of adequate

dissolving capacity at elevated temperature and rather low at room temperature.

Ethyl alcohol and carbontetrachloride possess these properties. The advantage of the former is that it is less toxic, and of the latter, is that it is virtually nonflammable.

TNT dissolves rather well in sulfuric acid (see Table 20). The high solubility of α -trinitrotoluene in sulfuric acid is an unfavorable property upon nitration, inasmuch as when TNT is separated from spent acid by separation, a portion remains in solution.

Table 20

a)	b)						
	70	75	80	85	90	95	100
0	—	0,30	0,40	0,6	2,0	3,5	13,0
10	—	0,30	0,45	0,7	2,2	4,0	13,5
20	—	0,30	0,50	0,8	2,5	4,8	15,0
25	—	0,32	0,55	0,9	2,6	5,2	15,5
30	—	0,35	0,60	1,0	2,7	6,0	16,5
40	0,2	0,40	0,65	1,3	3,0	7,0	18,0
50	0,2	0,45	0,70	1,7	3,5	8,5	21,0
60	0,22	0,50	1,00	2,3	5,2	11,0	24,0
70	0,35	0,70	1,60	3,3	7,0	13,5	29,0
80	0,60	1,30	2,40	4,8	10,0	18,0	36,5

a) Temperature, °C; b) Percentage solubility of α -trinitrotoluene in sulfuric acid of various percentage strengths

When a small amount of nitric acid is added to sulfuric acid, the solubility of α -trinitrotoluene in the resultant mixed acids diminishes somewhat (Bibl.37). However, larger quantities of nitric acid in acid mixtures have the opposite effect, increasing the solubility of α -trinitrotoluene.

Figure 23 presents a graphic illustration of the solubility of α -trinitrotoluene

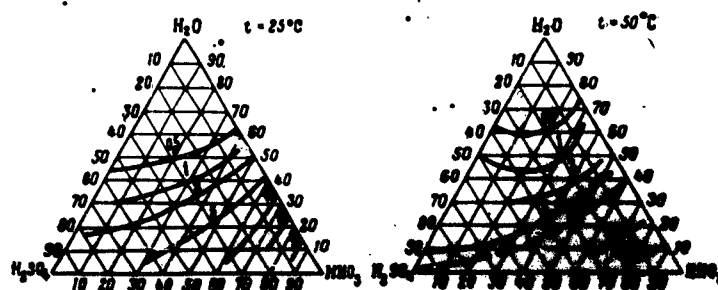


Fig.23 - Percentage Solubility of α -Trinitrotoluene (α -TNT) in Mixed Acids at 25 and 50°C

91 in mixed acids, in accordance with the composition of the latter, at 25 and 50°C.

92 The solubility of α -trinitrotoluene in nitric acid is very high, even in the case of dilute acid (see Table 21). This property is employed in engineering in the purification of technical TNT by recrystallization from nitric acid.

Table 21

a)	b)	c)	d)	e)	f)
78,2	48	100	84,7	33	100
	53	150		41	150
	56	200		46	200
	59	250		54	300
	61	300			
80,4	44	100	91,8	26	150
	50	150		34	200
	54	200		45	300
	56	250		55	500
82,5	38	100	97	34	235
	46	150		47	376
	50	200		52	458
	54	250		57	650
	56	300		61	830

a) Percentage strength HNO_3 ; b) Temperature °C; c) Solubility, gms of α -TNT (in 100 gm HNO_3)

α -TNT is of low reactivity, and this is a great advantage thereof as an explosive.

As a neutral substance, it does not react with the metal of the shell, and its low reactivity makes it possible to use it in mixtures and alloys with other substances, such as ammonium nitrate. This last circumstance makes it possible to increase the amount of explosives by using TNT-base mixtures and alloys.

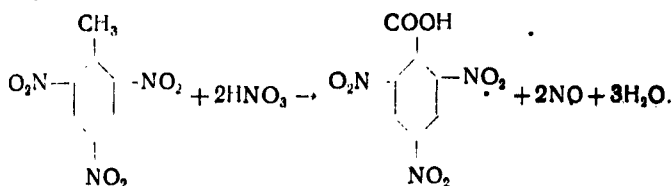
α -Trinitrotoluene forms a eutectic with tetryl. The eutectic contains 70.9 molar percent α -TNT and melts at 68.82° (Bibl.38), and also forms one with 2,4,6-trinitro-meta-xylene, containing 17.9 molar percent α -TNT, and melting at 78.7° (Bibl.39).

The melting points of various α -TNT-trinitrophenol mixtures may be found in Bibli.40.

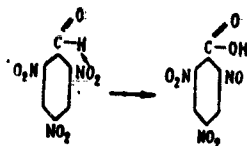
The behavior of α -TNT with various chemical reactants differs. Thus, strong sulfuric acid, which dissolves α -TNT at room temperature, does not react with it.

IX At high temperature, the TNT undergoes ~~XXX~~ oxidation. Thus, heating of 10 gm TNT with 10 gm strong sulfuric acid at 155° results in some gas formation, with liberation of SO₂. After 3.5 hrs of heating, the TNT remains unchanged, but takes on a light brown coloration. When this same reaction is run in a sealed tube, pronounced decomposition of the TNT sets in after 3.5 hrs, the tube bursts, and all that remains of the TNT is a sooty mass. At 145°, decomposition begins only after 6 hrs. These experiments show that a weak reaction between TNT and sulfuric acid at elevated pressure is capable of increasing greatly and ~~XXXXXXXX~~^{ending} with complete decomposition.

Strong nitric acid not only dissolves α -TNT, but even at 110°, slowly oxidizes it to trinitrobenzoic acid, in accordance with the equation:



It is entirely probable that the ~~XXXXX~~ oxidation process goes through the stage of trinitrobenzaldehyde formation. The further transformation of the aldehyde group into the carboxyl group may occur in the absence of oxidiser. We know, that due to their high reactivity, the nitrobenzaldehydes tend toward oxidation-reduction intramolecular processes, as a consequence of which nitrobenzoic acids are formed. Consequently, the following reaction may occur in this situation



in the final KI analysis what will result, evidently, is not dinitronitrobenzoic acid, but its dimer, attached through the nitroso group thanks to the high reactivity thereof (Bibl.41).

At high temperature (115 - 130°), strong mixed acid oxidizes α -TNT, with destruction of the benzene ring. The oxidation product, in addition to gases, is tetranitromethane $C(NO_2)_4$.

α -TNT does not react with water either when cold or upon heating.

The acquisition of a red color by TNT, accompanied by an increase in oiliness, which occurs under conditions of industrial washing of the product, is apparently induced by the considerable overheating of TNT containing admixtures of ~~AKH~~ asymmetrical trinitrotoluenes when ~~AKH~~ subjected to the direct effect of live steam and high temperature (of the order of 150°). The hardness of the water has a major effect upon the reddening of the TNT, upon washing. Calcium salts in the water form dark brown metallic derivatives with TNT. These derivatives decompose upon boiling, with formation of condensation products.

α -TNT reacts with aqueous and alcoholic solutions of bases to form metallic derivatives, dark brown in color, ~~erroneously~~ erroneously termed trotylates, because this term should be applied to salts of trotyl and a base, whereas this is not the structure of the metallic derivatives of TNT.

Colorimetric qualitative and quantitative methods (Bibl.42, 43) of determining

α -TNT and others of its isomers are based upon the reaction with caustics.

The qualitative reaction is performed as follows: 1 cc 0.01% alcoholic solution of nitro compound with 4 cc acetone and one drop 2n · NaOH yields a color characteristic for each isomer of TNT, as shown in Table 22.

Metallic TNT derivatives are most readily obtained by the action of potassium or sodium alcoholate upon a solution of TNT in toluene.

94 Studies (Bibl.44,45) have shown that as many as three molecules of the alcoholate (CH_3OK) may attach to one molecule of α -TNT in Et_2O an anhydrous medium. According to Meisenheimer (Bibl.46) the alcoholates^{all} of quinoid structure:

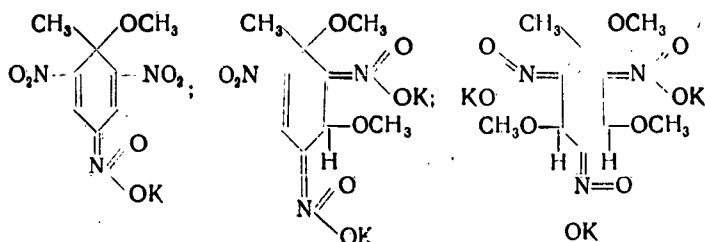


Table 22

Isomers of TNT	Color Observed		Remarks
	Immediately after Pouring	5 min later	
α (2,4,6)-	Deep red	Deep red with slightly dirty tint	Carmine after 15 min; pink after 30 min; pale pink after 45 min
γ (2,4,5)-	Bluish gray	Gray	Pale gray after 15 min.
β (2,3,4)-	Green	Pale yellow, and slightly reddish	After 30 min, yellow
η (2,3,6)-	Pinkish white	Almost colorless	After 30 min, colorless
δ (3,4,5)-	Bright violet	Bright violet	After 20 min, pale brown; after 30 min, pale yellow
ϵ (2,3,5)-	Carmine red	Carmine red	After 15 min, pale red

The metallic derivatives of α -TNT are explosives having a considerably lower flash point and higher shock sensitivity than α -TNT. As the number of molecules of the alcoholate attached increases, the flash point of the metallic derivatives is reduced, inasmuch as for ~~XXXXXXXXXX~~ monometallic compound it is 148° , and for a trimetallic it is 117° .

These substances are exceedingly unstable. I.V.Stefanovich (Bibl.44) has observed cases in which, when a substance of the composition $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot 2\text{C}_2\text{H}_5\text{OK}$ was heated in a thermostatic container, it exploded at 50° after 15 min of heating, whereas compound $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot 3\text{C}_2\text{H}_5\text{OK}$ exploded at 55° after 20 min of heating.

~~XXXXXXXXXX~~ shock sensitivity
The ~~XXXXXXXXXX~~ of the metallic derivatives of α -TNT ~~XX~~ is equal to that of initiating explosives.

The metallic derivatives of α -TNT are hygroscopic and run in air. When they are subjected to dilute mineral acids, the α -TNT is not recovered, as is the case with trinitrobenzene, but nitrogen oxides and deep red (almost black when dry) products insoluble in water, benzene and ether, but readily soluble in alcohol, are liberated. These black ~~XXXXXXXXXX~~ products vary in composition, depending upon the strength and properties of the acids, and also upon the length of time the acids have been at work. The flash point is $220 - 260^{\circ}$, and their shock sensitivity is similar to that of lead azide. It is held that when mineral acids react with metallic derivatives of α -TNT, what occurs is the nitromolecular oxidation of the CH_3 group at the expense of the oxygen of the NO_2 group and subsequent condensation of the oxidised modules into more complex compounds, dibenzyl derivatives.

Aqueous solutions of the caustics act upon α -TNT in a somewhat different manner.

Whereas the effect of sodium alcoholate upon the toluene XX solution of α -TNT results in metallic derivatives ~~XXXXX~~ being liberated in the form of a precipitate of constant compositions, when an aqueous solution of caustic acts upon α -TNT, the latter dissolves slowly therein to form a dark solution. After the water has evaporated, a brown (almost black) substance of unknown composition remains of the solution, as the caustic that does not go into reaction cannot be washed away without subjecting the product to a destructive reaction.

The mechanisms of the reactions between aqueous caustics and nitro compounds have XX had inadequate study. It has been established that a series of reactions follow rapidly one upon the other. Reactions of formation of additive compounds, substitution products, and condensation products may occur simultaneously or one XX after the other (Bibl.47).

An investigation of the explosive properties of the reaction products of α -TNT with an aqueous solution of KOH show that the flash point fluctuates between 104° and 157° , depending upon the amount of caustics, and the shock sensitivity is greater than that of lead azide.

α -TNT reacts not only with strong caustics, but with so weak a one as NH_4OH .

I.V.Stefanovich has obtained ammonium derivatives in two ways: by dissolving α -TNT in an ~~XXX~~ aqueous solution of ammonia or by mixing a toluene solution of α -TNT and an alcohol solution of ammonia. When the ammonia derivatives XX are dried in a desiccator over sulfuric acid, liberation of nitrogen oxides is observed, testifying to the instability of these compounds.

Solid α -TNT also reacts with gaseous ammonia. The process is accelerated in the presence of moisture and when temperature is reduced (Bibl.44,48). If α -TNT is placed

in a vessel with gaseous ammonia, the ammonia is absorbed, and the properties of the α -TNT undergo a pronounced change. First it turns red, then it acquires a darker and darker coloration, and finally is converted into a thick-black-tarry substance, which transforms into a porous substance after ~~the~~ desiccation. This substance does not explode upon shock and burns with difficulty upon calcination. The intermediate product from the reaction of α -TNT with gaseous ammonia is highly sensitive to shock and has a low flash point ~~XXXXXX~~ (110°).

The question of the formation of metallic derivatives of α -TNT is not only of theoretical but of ~~the~~ major practical significance. Previously, soda solutions were employed to wash TNT, and alloys of TNT with potassium and ~~XXXXXX~~ sodium nitrate were employed along with ~~XXXXXX~~ ammotols. In 1916, an explosion occurred at a plant where TNT was being fused with potassium nitrate. The conclusion of an expert commission was that the explosion occurred as a consequence of the formation of a particularly sensitive metallic derivative of TNT (Bibl.49).

The shock sensitivity of the ammotols increases very significantly with the length of time for which shells filled with them have been stored. Along with the increase in the shock sensitivity of the ammotols, there are cases on record of flash at low temperature. Ammotol-filled shells remaining at the close of the war were emptied. Cases of ignition and burning were noted at times ~~XXXXXX~~ during the steam melting out of the ammotols. The increased shock sensitivity and the reduced flash point of ammotols is to be explained by the formation of compounds of TNT and ammonia, which may form from the NH_4NO_3 upon reaction with the metal shell case. To avoid the formation of dangerous ~~the~~ compounds of TNT and ammonia when shells are filled with ammotol, the ammotol must be thoroughly insulated from contact with the metal of the shell

casing and the fuse, by means of lacquer or a cartridge type of filling.

A study of the causes of ignition occurring in the manufacture of TNT (Bibl.50) showed that when lead and iron act upon TNT in the presence of nitric acid, explosive metallic compounds come into being. Aluminum also yields compounds of this type, but these are less sensitive to ignition. The presence of such salts in TNT shops may be the cause of accidents.

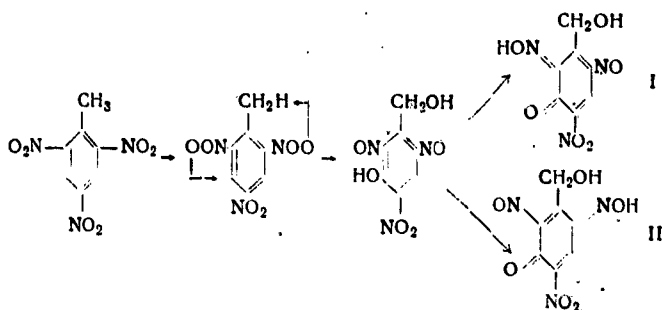
Sunlight affects α -TNT, causing it to darken and change in properties (primarily, the freezing temperature). This is apparently due to photoisomerization [the effect of ultraviolet rays upon α -TNT (Bibl.51)].

Light has a less pronounced effect upon the flash point. A product of the irradiation of α -TNT with light has a flash point of 230° , and 76% shock sensitivity, i.e., its sensitivity is greater than that of tetryl.

G.Schultz and K.Ganguli (Bibl.52), who subjected TNT to long-term solar irradiation, derived a "red dye" (it will dye wool) therefrom, constituting a mixture of two substances, one of which is a hygroscopic brown powder readily soluble in ~~the~~ cold water and cold acetone ~~and not soluble in ether, benzene,~~ and chloroform; the other a black amorphous powder which dissolves with greater difficulty in water and does not dissolve in acetone and other organic solvents. Both substances have the same ~~the~~ elementary composition and molecular weights as TNT. From this, the authors draw the conclusion that both substances are products of intramolecular regrouping of 2,4,6-TNT, which would appear to be correct, as the same substances ~~have been~~ obtained ~~by~~ upon irradiation of TNT by solar or ultraviolet light in an atmosphere of oxygen, hydrogen, nitrogen, and in vacuum. These substances are apparently isomeric, as their absorption spectra ~~are~~ are virtually identical, and the brown substance

gradually converts to the black when dissolved in acetone. All this provides reason to assume that when light acts upon α -TNT, photoisomerization thereof occurs. This involves the formation of quinoximes and nitrosophenols as a consequence of a shift of the oxygen of the nitro group in the ring.

Photoisomerization occurs at the expense of the nitro groups in the ortho position, with formation of two isomeric compounds in accordance with the following mechanism



I - are derivatives of ortho-quinoxime: 4-nitro-2-nitroso-1-oxymethyl-5,6-benzoquinone-6-oxime (insoluble in cold acetone);

II - is a derivative of para-quinoxime: 4-nitro-6-nitroso-1-oxymethyl-2,5-benzoquinone-2-oxime (soluble in cold acetone).

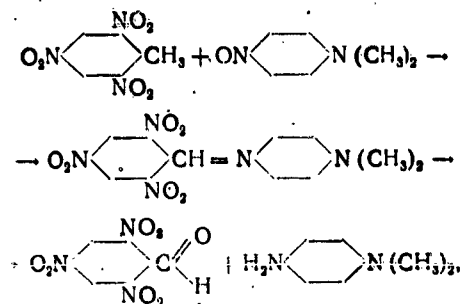
The phenomenon of photoisomerization proceeds exclusively at the expense of the nitro groups which are in the 2 and 6 positions. This is proved by the fact that in the dinitrotoluene series, only the 2,6-isomer yields, in a manner analogous with α -TNT, to products of reaction with solar light similar thereto.

Pavlik (Bibl.53), accepting the view of Schultz and Ganguli as his starting data contends that the absorption spectra of substances formed from TNT as a consequence of the action of light, heat, sulfites, and caustics, are very similar, and that this similarity is apparently due to the similarity of their chemical structures.

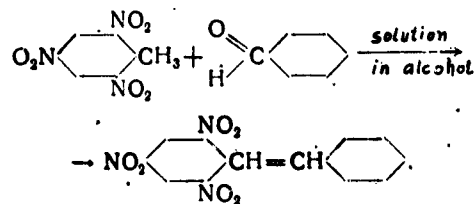
The capacity of TNT to undergo isomerization under the influence of sunlight, the formation with ~~formation~~ of sensitive compounds, is merely of theoretical interest, inasmuch as, in practice, TNT is not subject to the effect of light, as it is usually housed in some object or sealed up.

α -TNT is capable of reacting, via the methyl group (which is more active therein than in asymmetrical isomers), with a series of compounds (Bibl.54), as, for example,

para-nitroso-dimethylaniline and benzaldehyde. In the former instance the ~~main~~ consequence is trinitrobenzaldehyde:



and in the latter, trinitro derivatives of stilbene:



Like other nitro compounds, TNT is poisonous and the proper safety regulations have to be observed in working with it (Bibl.55).

Explosive properties of TNT (Bibl.35). Purified troyl is virtually chemically pure α -trinitrotoluene. It is a good explosive: physically and chemically stable, readily subject to pressing, and yielding castings of high quality.

Its basic explosive properties are as follows:

Shock sensitivity	4 - 8% explosions (at p = 10 kg, h = 25 cm, and a sample of 0.05 gm; explodes upon the dropping of a 2 kg weight from a height of 100 cm)
Flash point*	290°
Expansion in Transl block	285 cc
Brisance:	
due to Hess	16 mm
due to Kast	3.9 mm
Velocity of detonation ($\rho = 1.62$)	7000 m/sec

The volume of the gaseous explosion products is 730 ltr/kg, the ~~HEAT~~ heat of explosion 1010 kcal/kg, and the temperature of explosion 3100°C.

The sensitivity of pressed TNT to detonation is ~~HEAT~~ satisfactory. The limit of the initiation charge of mercury fulminate for pressed TNT is 0.38 gm. Cast TNT is considerably less sensitive to detonation. It cannot be detonated by a ~~HE~~ No. 8 detonating cap, and therefore intermediate detonators are used to explode it.

In the pure form, TNT is employed to fill artillery shells and aviation bombs as well as to prepare sapping materials and intermediate detonators.

In Germany certain type shells ~~HEAT~~ of medium and large caliber (armor-piercing and concrete-piercing) were loaded by the multiple-cartridge method with phlegmatized TNT.

TNT is widely employed in the form of alloys with other explosives, primarily ~~HEAT~~, as well as with dinitronaphthalene. Mixtures of TNT and ammonium nitrate are the most widely employed both for military and for peacetime purposes. For the filling of special munitions, specifically, for shaped charges and mines, ~~HEAT~~ ^{mixtures} of TNT

*In accordance with the data of ~~HEAT~~ Bibl.35, 475°. In this case, the temperature of detonation was taken at the temperature that would induce detonation within 5 sec.

The process of producing TNT consists of the following stages:

- a) nitrating toluene to TNT;
- b) washing the TNT free of acid with water;
- c) freeing the TNT from impurity;
- d) drying the TNT.

A distinctive characteristic of virtually all stages in the manufacture of TNT is the liquid state of the intermediate products and the products in the process of production, as a consequence of the fact that they are carried out at high temperatures higher than the melting points of the substances referred to.

a) Nitrating Toluene to TNT

Nitration of toluene to mononitrotoluene (Bibl.12, 20, 56, 57, 58, 59). Study of the reaction of nitration of toluene to mononitrotoluene has been directed chiefly to reducing the yield of meta-nitrotoluene, so as subsequently to obtain TNT with minimum impurities. Investigations have also been made of various characteristics of the nitration of toluene under heterogeneous conditions: solubility, distribution of the components in the various layers, effect of stirring upon reaction speed, etc.

The solubility of toluene in sulfuric acid of various strengths at 55° is illustrated in Fig.24 from which it is seen that at acid strengths of less than 80% H_2SO_4 , the solubility of toluene is very low, and inasmuch as nitration thereof is usually conducted with an acid mixture containing more than 20% water, it consequently occurs under heterogeneous conditions with low solubility of the toluene in the mineral layer.

The velocity of toluene nitration under heterogeneous conditions is highly dependent upon the rate of agitation, and the modulus M (the ratio of the volumes of the mineral and organic phases). The effect of the intensity of agitation K upon

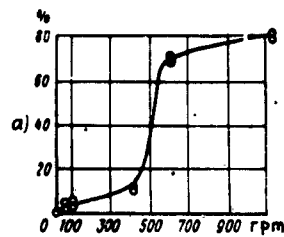
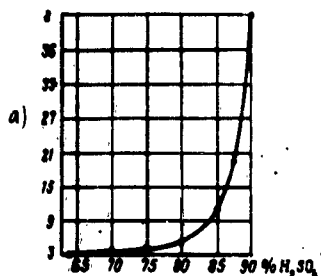


Fig. 24 - Solubility of Toluene in Sulfuric Acid of Various Strengths K at 55°
 Fig. 25 - Influence of Intensity of Agitation upon Toluene Nitration Velocity
 a) Yield of mononitrotoluene

a) Toluene dissolved in 100 gm acid

the degree of nitration of toluene (at a temperature of 30°C and a modulus of 3) by a mixed acid of the composition: 64% H₂SO₄; 11% HNO₃; 25% H₂O, and having a factor of

nitrating activity K f.n.a. = 69% and 30 min.

nitration time, is illustrated in Fig. 25. The

effect of the modulus upon the degree of

nitration of the toluene (at temperature 30°C

with a mixed acid of composition: 55% H₂SO₄;

27% HNO₃; 18% H₂O, with K f.n.a. = 68%, and

50 min nitration time) is illustrated in Fig. 26.

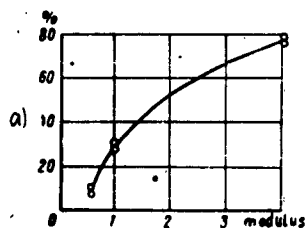


Fig. 26 - Effect of Modulus upon Velocity of Toluene Nitration
 a) Yield of mononitrotoluene

Figures 25 and 26 show that the higher the

intensity of agitation, and the greater the volumetric share of the inorganic layer,

the higher the toluene nitration reaction velocity.

The coefficient of ~~XXXXXXXX~~ distribution of nitric acid between the toluene and sulfuric acid layers (at 5°C and 70% H₂SO₄) is 0.066, but with weaker H₂SO₄ it is zero. This testifies to the fact that in heterogeneous nitration of toluene, nitric acid enters the organic layer to only a negligible degree, and therefore the portion of the reaction occurring there is practically equal to zero.

The low solubility of the toluene in moderate strength sulfuric acid, the fact that the nitric acid does not enter the organic layer, and the pronounced dependence of the toluene nitration reaction velocity upon the intensity of agitation and the volumetric share of the mineral layer make it possible to assume that the toluene nitration reaction in heterogeneous conditions occurs near the interface between the layers. In this case, the velocity will be determined by the strength of the reacting components at this surface, and this in turn is determined by the rate of diffusion of the reacting components from the depth of the layer to the interface, and the rate at which the reaction products move away from it.

These processes, as well as the state of the reacting component, depend upon the temperature, the strength of the mixed acid, and the intensity of mixing. The dependence of the ~~XX~~ toluene nitration rate upon temperature (time 30 min, f.n.a. 70.9%, modulus 7.9) is illustrated in Fig.27, ~~XXXX~~ while its dependence upon the factor of nitrating activity of the mixed acid (at temperature 55° and 30 min time) is shown in Fig.28.

A change in the factor of nitrating activity from 64.5 to 74% results in a change in the velocity by a factor of 2.2. A comparison of the toluene nitration reaction

velocities in heterogeneous and homogeneous conditions show that the reaction of velocity in heterogeneous conditions is less than in homogeneous conditions. Thus,

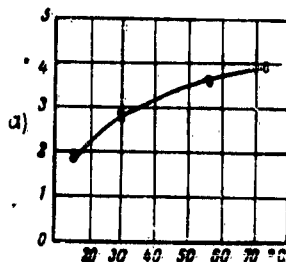


Fig. 27 - Effect of Temperature upon Toluene Nitration Velocity

a) Nitration velocity in $\frac{\text{gm-mole}}{\text{ltr/min}}$

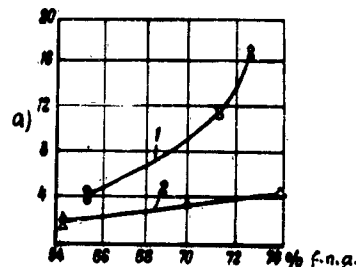


Fig. 28 - Effect of Factor of Nitrating

Activity (f.n.a.) of the Mixed Acid upon the Toluene Nitration Velocity

1) Nitration in homogeneous medium; 2) In heterogeneous medium

a) Nitration velocity in $\frac{\text{gm-mole}}{\text{ltr/min}}$

for a mixed acid in which f.n.a. = 73% at 55°, the reaction velocity is less by a factor of four.

The manufacture of TNT is ~~more~~ complicated in the first stage of nitration by the undesirable formation of meta-nitrotoluene. The formation of 5 - 6% of this isomer leads subsequently to formation of 5 - 6% of asymmetrical TNT, contaminating the TNT.

Table 24 illustrates the relationship of the freezing point of TNT to the ~~percentage~~ asymmetrical isomers derived from meta-monomitrotoluene (Bibl.11) it contains.

The freezing point of TNT is reduced by the asymmetrical isomers present in accordance with the following relationship: $t_{\text{freez}} = (80.80 - 0.465c)$, where c is the percentage content of meta-nitrotoluene in the initial mononitrotoluene.

Table 24

Meta-mononitrotoluene added, %	0	2.11	3.22	4.86	8.78
Freezing point of TNT, °C	80.80	79.87	79.26	78.70	78.13

101

Investigations have shown that the yield of meta-nitrotoluene may be reduced:

a) by reduction of the temperature of nitration (see data of Table 25 and Fig.29),

illustrating the influence of the temperature upon the isomeric composition of the

mononitrotoluene in the nitration of toluene by mixed acid in which f.n.a. = 72.5%,

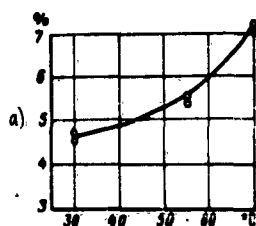


Fig.29 - Effect of Temperature upon Yield of Meta-Nitrotoluene (m-MNT)

a) Yield m-MNT

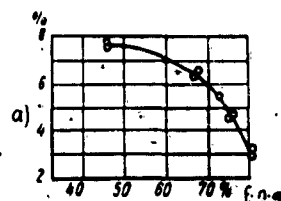


Fig.30 - Effect of Factor of Nitrating Activity (f.n.a.) upon Yield of Meta-Nitrotoluene (m-MNT)

a) Yield m-MNT

(for 100 min). Reduction in temperature from 70° to 30° results in a reduction in the yield of meta-nitrotoluene by a factor of 1.6;

Table 25

Temperature, in °C	30	55	70
Percentage composition of mononitrotoluene			
para-	35.0	34.9	32.3
meta-	4.6	5.3	7.5
ortho-	60.4	59.8	60.2

b) upon increase in the factor of nitrating activity of the mixed acid, (Fig.30 illustrates the effect of the f.n.a. upon the yield of meta-nitrotoluene when toluene is nitrated for 100 min by a mixed acid containing 10% HNO_3 at a temperature of 55°); when the f.n.a. is raised from 68% to 82.7%, the yield of meta-nitrotoluene is reduced by a factor of 2.4;

c) upon introduction of sodium nitrite into the mixed acid (data of Table 26 and

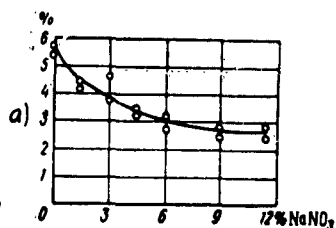


Fig.31 - Effect of Sodium Nitrite upon Yield of Meta-Nitrotoluene (m-MNT)

a) Yield of m-MNT

Fig.31, where the effect of the quantity of NaNO_2 upon the yield of meta-nitrotoluene in nitration of toluene by mixed acid, with f.n.a. = 73% containing 10% HNO_3 at 55° , for 100 min, is shown); addition of sodium nitrite induces a reduction in the amount of meta-nitrotoluene by nearly 50%.

The optimum quantity of sodium nitrite making

it for the production of TNT having the maximum

freezing point of 79° in further nitration of mononitrotoluene to TNT, is about 6%.

A further increase in the addition of ~~III~~ sodium nitrite results in the appearance of oxidation products and nitration products in the TNT side chain, resulting in reduction of the freezing point of the TNT.

The effect of sodium nitrite upon the yield of meta-nitrotoluene may be explained in terms of the concepts of Brown and others (Bibl.60) who held (true, for alkylation) that the quantity of meta-isomer formed is characterized by the selectivity of the effect of the substitute group attacking the toluene. Moreover, the more active the

Table 26

NaNO ₂ in %	0	1.5	3.0	4.5	5.0	7.2	8.0	11.0
Percentage yield of meta-nitrotoluene	5.4	4.3	4.1	3.5	2.8	—	2.7	2.6
Freezing point, in °C, of TNT	78.0	78.60	78.75	78.75	78.90	78.45	78.30	77.9

reactance, the greater the degree to which substitution in the meta position occurs.

However, the activity of the H^+ attacking reactant is determined by the degree to

which it is electrophilic. If it be taken that, upon ~~addition~~ ^{addition} of NaNO₂, the

nitration of toluene will proceed not only due to the NO₂⁺ cation ~~(formed from~~ ^{(formed from}

the HNO₃), but due to the NO⁺ and NO₂ (formed from NaNO₂), then the reaction with

the latter, as the less electrophilic ~~reactance,~~ ^{reactance,} must result in a smaller yield of

meta-nitrotoluene.

As a consequence of these investigations, the following regularities have been

established for the process of nitration of toluene to mononitrotoluene, under

heterogeneous conditions:

a) The process rate is apparently determined by the rate of diffusion of the components in the reaction zone, inasmuch as nitration occurs primarily at the layer interface;

b) The nitration rate under heterogeneous conditions is comparatively little dependent upon temperature, while at the same time, the yield of meta-nitrotoluene diminishes with reduction in temperature. Consequently, it is desirable to nitrate the toluene at low temperature. This will facilitate a reduction in the yield of meta-nitrotoluene, and will have comparatively little effect upon the rate of

nitration;

c) An increase in the factor of activity of the mixed acid for reduction in the meta-nitrotoluene content, and an increase in the quality of the raw TNT;

d) It is desirable to make use of the most intensive agitation, with the object of increasing reaction rate, particularly under low-temperature conditions of nitration. This results in an increase in the productivity of the system.

mononitrotoluene

Nitration of ~~XXXXXXXXXXXXXXXXXXXX~~ to dinitrotoluene (Bibl.58, 59, 61).

as

Little attention has been given to ~~the~~ investigation of the reaction of nitration

mononitrotoluene

of ~~XXXXXXXXXXXXXXXXXXXX~~ to dinitrotoluene. This is understandable, to some degree, inasmuch as, in the production of TNT, this stage is an intermediate link between the first and third stages. ~~XXXXXXXXXX~~ Mononitrotoluene comes to this stage from the first stage, and sulfuric acid in the form of spent acid comes to it from the third stage. Nitration of mononitrotoluene to dinitrotoluene is usually performed with the utilization of all the spent acid from the third stage, and with strong or weak nitric acid. This stage presents no great difficulty in the production process.

In a work by Kobe and associates (Bibl.61), a study was performed of the influence of ~~XXXX~~ various factors upon the nitration of the ortho- and ~~XXXX~~ para-nitrotoluenes ~~XXXX~~ to dinitrotoluenes. They determined that ~~XXXXXX~~ ortho- and para-nitrotoluenes undergo nitration at virtually identical velocity.

Under optimum process conditions, the yield of dinitrotoluene from ortho-nitrotoluene is 100%, and that from para-nitrotoluene is 96%. The optimum conditions are the following:

	Ortho-nitro- toluene	Para-nitro- toluene
--	-------------------------	------------------------

Number of parts at H ₂ SO ₄ per part of mononitrotoluene	1.25-1.75	1.75
Percentage strength of H ₂ SO ₄ in %	85	85
Temperature, in °C	15-20	15-20
Reaction time in minutes		

103 Figure 32 shows the effect of the MX amount of 90% sulfuric acid upon yield of dinitrotoluene. Figures 33 and 34 show the temperatures and strengths of sulfuric acid, and Fig.35 shows the time and temperature (nitration, in the last of these cases, was performed in a medium of 80% H₂SO₄).

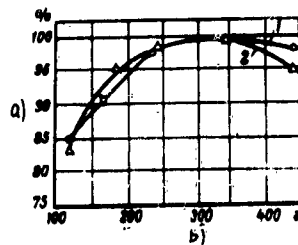


Fig.32 - Effect of Amount of 90% Sulfuric Acid upon a Yield of Dinitrotoluene (DNT). Nitration of the individual isomers of mononitrotoluene (MNT).
1 - n-MNT; 2 - o-MNT
of
a) Yield/DNT; b) Quantity of H₂SO₄

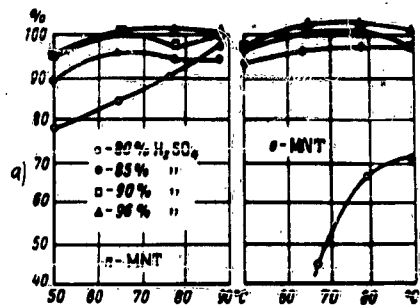


Fig.33 - Effect of Temperature upon Yield of Dinitrotoluene (DNT). Nitration of ortho- and para-mononitrotoluene (MNT) in a medium of sulfuric acid of various strengths
a) Yield of DNT

A.G.Gorst and A.I.Trufanova have determined the following ~~REGULARITIES~~ regularities in heterogeneous nitration of para-nitrotoluene.

The nitration of para-nitrotoluene goes at noticeable speed at 70°/performed when with mixed acid in which the factor of nitrating activity is 72%. An increase therein to 79.84% increases the velocity five-fold (the data in Table 27 and Fig.36 are

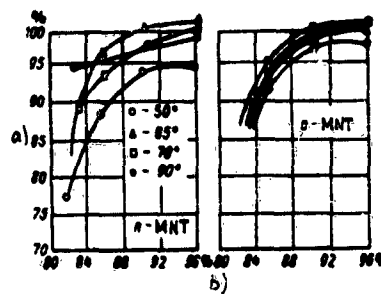


Fig.34 - Effect of Strength of Sulfuric Acid upon Yield of Dinitrotoluene (DNT). Nitration of Ortho- and Para-Mononitrotoluene (MNT)

a) Yield of DNT; b) Strength of H_2SO_4

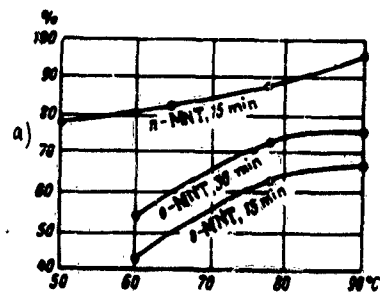


Fig.35 - Effect of Temperature upon Yield of Dinitrotoluene (DNT). Nitration of Ortho- and Para-Mononitrotoluene (MNT)

a) Yield of DNT

descriptive of the influence of the factor of nitrating activity of the mixed acid upon the nitration velocity of para-nitrotoluene at 70°).

Figures 37 and 38 present the relationship between the nitration velocity of para-nitrotoluene and the temperature and intensity of agitation. The nitration of para-nitrotoluene was performed by a mixture of the following composition: 73% H_2SO_4 ; and 4% HNO_3 ; 23% H_2O , for 30 min. In the first instance, the temperature changed; in the second it was constant (70°).

The data of these experiments show that the reaction velocity of nitration of mononitrotoluene under heterogeneous conditions depends, as does that of toluene, upon the intensity of agitation (the size of the layer interface). However, this relationship is somewhat less distinct than in the case of toluene.

Table 27

a)	71.83	74.07	75.92	77.77	79.84
$\frac{4m-nol}{t \cdot f_{min}} \cdot 10^{-3}$	16,3	42,9	60,6	74,4	85,0
b)	17,8	46,5	65,1	78,7	88,8

a) Factor of nitrating activity in %; b) Quantity of nitrated mononitrotoluene, %

The relationship of the nitration velocity of mononitrotoluene \bar{M} under heterogeneous conditions to the intensity of agitation ~~testifies~~ testifies to the fact that nitration occurs, to a considerable degree, in the vicinity of the interface. In addition, nitration occurs in the mineral layer, where the concentration of mononitrotoluene under the conditions of this process is sufficiently high (see the solubility of mononitrotoluene in sulfuric acid, p.162).

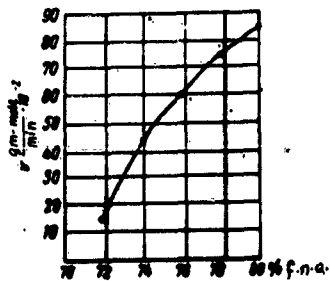


Fig.36 - Effect of Factor of Nitrating Activity of Mixed Acid (f.n.a.) upon Nitration Velocity of Para-nitrotoluene at 70°

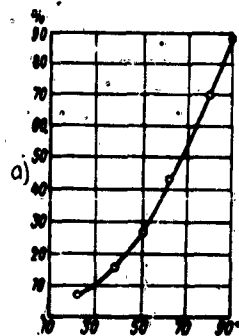


Fig.37 - Effect of Temperature upon Para-nitrotoluene (MNT) Nitration Velocity
a) Quantity of nitrated MNT

Nitration of dinitrotoluene to trinitrotoluene (Bibl.59, 62, 63, 64, 65).

The nitration of dinitrotoluene is the slowest stage in the process of producing TNT, as a consequence of the pronounced ~~addition~~ ^{enters,} ~~rate~~ ^{the speed at which a third nitro group} in addition to the two nitro groups already in ~~the~~ benzene ring, ~~of this process with the addition of a third nitro group~~. This is clearly evident on the basis of the nitration of dinitrotoluene by strong nitric acid, which reacts with it at an insignificant velocity. An increase in temperature has little effect upon this velocity, it only makes for the development of powerful oxidizing properties (Bibl.62, 65). The mixed acids, particularly strong mixtures, nitrate the dinitrotoluene at a higher rate than does pure nitric acid alone.

The nitration reaction velocity under homogeneous conditions depends upon the concentration of sulfuric acid, and, according to Bennett and Brand (Bibl.63) follows the regularity illustrated in Fig.39. The authors perform nitration of 0.4 mole of dinitrotoluene by 0.2 mole of HNO_3 dissolved in 16.8 moles of H_2SO_4 of various strengths at 90° .

According to studies by Ye.In.Orlova (Bibl.59, 65), this ~~regularity~~ regularity changes as the strength of the HNO_3 in mixed acid rises. As we see from Fig.40, the rate of nitration of dinitrotoluene taken in a quantity of 0.70 mole, by 3.8 moles of HNO_3 , dissolved in 12 moles H_2SO_4 increases when one converts from the use of 87% to 100% H_2SO_4 . There is no nitration velocity maximum in this range of acid strengths.

It is not difficult to demonstrate by computation that, in mixed acids having a large amount of HNO_3 , only a portion thereof converts to the active nitrating

from NO_2^{\oplus} . With the increase in strength of the H_2SO_4 , the share of NO_2^{\oplus} increases, and the nitration velocity rises. Under these conditions, the nitration velocity maximum apparently shifts into the region of higher sulfuric acid strength.

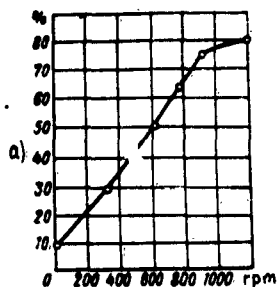


Fig.38 - Effect of Intensity of Agitation upon the Rate of Nitration of para-Nitrotoluene (MNT)

a) Quantity of nitrated MNT

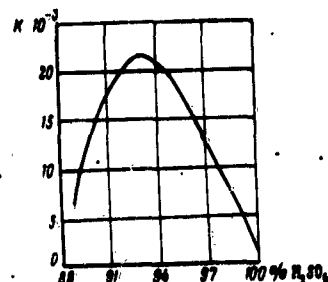


Fig.39 - Effect of Concentration of Sulfuric Acid upon the Rate of Nitration of Dinitrotoluene under Homogeneous Conditions (Sulfuric Acid with Low Content of HNO_3)

In the production of TNT, the nitration of dinitrotoluene, like that of toluene and mononitrotoluene, occurs under heterogeneous conditions. In this situation, the process rate consists of the rates of the processes of diffusion of the reacting components from one layer to the other, and then of nitration. The total velocity is determined by the velocity of the slower process. If the velocity of nitration is higher than the velocity of diffusion, the reaction will usually occur at the interface, as takes place in the case of nitration of toluene and mononitrotoluene. At low nitration velocity, reaction will occur within that

~~XXXX~~ layer in which ~~XX~~ reactant components exist.

It is evident from Fig.41 that the velocity at which dinitrotoluene is nitrated under heterogeneous conditions is above some specific figure and is

practically independent of the intensity of agitation (nitration was conducted for

40 min by a mixed acid of the following

composition: 81% H_2SO_4 , 16% HNO_3 , temperature 90° , and modulus 1.5). This permits one to

conclude that the bulk of the nitration of dinitrotoluene proceeds not at the interface, but within the layers. Agitation is necessary, however, to ease the diffusion of the reacting components in the reacting zone.

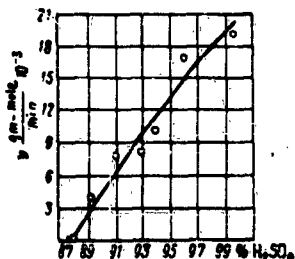


Fig 40 - Effect of Sulfuric Acid Strength upon Dinitrotoluene Nitration Velocity under Homogeneous Conditions (Mixed Acids with High HNO_3 Content)

Dinitrotoluene readily dissolves in sulfuric acid but the solubility of TNT therein is considerably poorer (data on solubility at 100° are presented in Table 28 and Fig.42.

106

The solubility of alloys of dinitrotoluene and ~~XXXXXX~~ trinitrotoluene lies between the solubilities of pure dinitrotoluene and pure trinitrotoluene, and depends upon the ~~XXXXXXXX~~ composition of the alloy. With increase in the TNT content, the solubility of the alloy ~~XX~~ diminishes. A substantial reduction in solubility is observed when 20 - 30% TNT is added to the dinitrotoluene. Further change in solubility occurs more smoothly, and solubility is reduced in proportion to the increase in the TNT content in the alloy. The solubility of the products depends

Table 28

a)	b)		
	87	91	98
100	10,7	21,5	54,0
76	9,0	16,0	38,0
55	8,7	14,7	30,4
35	7,7	12,0	25,7
16,6	6,9	11,5	22,5
0	6,1	10,6	19,7

a) Dinitrotoluene content in alloy with TNT, %; b) Solubility of alloy, %, in sulfuric acid of various strengths, %

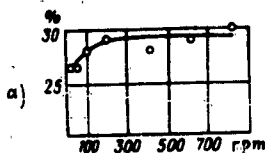


Fig. 41 - Effect of Intensity of Agitation ω upon Dinitrotoluene (DNT) Nitration Velocity
a) Amount of DNT nitrated

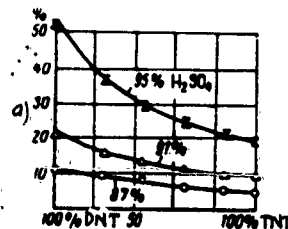


Fig. 42 - Solubility of Dinitrotoluene (DNT) and Alloys Thereof with Trinitrotoluene (TNT) in a Sulfuric Acid of Various Strengths
a) Dissolved

greatly upon the strength of the sulfuric acid and, to a considerably smaller degree, upon temperature.

When the dinitrotoluene - TNT alloy undergoes partial solution, the dinitrotoluene is distributed between the layers. Dinitrotoluene, as a product of high solubility, goes into the mineral layer in larger quantity than does TNT. Thus, the mineral layer becomes enriched in dinitrotoluene, when compared to the organic

layer. Nevertheless, the coefficient of distribution dinitrotoluene is very small (0.3 - 0.4), due to the low solubility of the alloys in sulfuric acid. This testifies to the ~~small~~ comparatively low strength of the dinitrotoluene in the mineral layer.

The relationship of the coefficient of distribution/dinitrotoluene and the solubility of a 50/50% dinitrotoluene - TNT alloy in 90% H_2SO_4 , relative to temperature, is illustrated in Table 29 and in Fig.43, whereas Fig.44 illustrates the effect of the strength of the sulfuric acid at 90° upon the coefficient of distribution.

The coefficient of distribution of nitric acid between the mineral and organic layers, when dinitrotoluene has been nitrated in 93% H_2SO_4 at 90° (see data in Table 30, presenting the influence of the amount of HNO_3 in the mixed acid upon the dinitrotoluene nitration velocity) is approximately equal to unity, and this testifies to the high degree of absorption of the nitric acid by the organic layer.

Table 29

Temperature in °C	70		80		85		90	
Dissolved alloy, %	16,8	18,2	19,0	17,9	19,3	19,3	18,0	19,0
Including:								
Dinitrotoluene	13,8	13,2	13,4	12,9	12,1	11,9	10,5	8,9
TNT	3,0	5,0	5,6	5,0	7,2	7,4	7,5	10,1
Coefficient of distribution (R)								
% dinitrotoluene in mineral layer	0,32	0,31	0,31	0,29	0,28	0,28	0,22	0,18
% dinitrotoluene in organic layer								

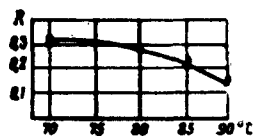


Fig. 43 - Effects of Temperature upon Distribution Coefficient R of Dinitrotoluene between Mineral and Organic Layers.

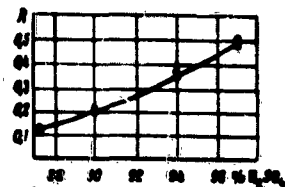


Fig. 44 - Effect of Strength of Sulfuric Acid upon Distribution Coefficient R of Dinitrotoluene between Mineral and Organic Layers.

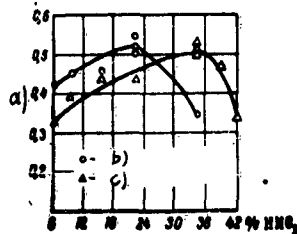
Table 30

Percentage of Nitric Acid in Mixed Acid	6,1	9,3	16,7	22,7	35,6	35,6	35,6	38,8	41,5	
Trinitrotoluene obtained g-mole ltr	Homogeneous condition		0,420	0,455	0,510	0,535	0,375	0,361	—	—
	Heterogeneous condition		0,326	0,394	0,450	0,435	0,550	0,535	0,524	0,492
Coefficient of distribution of HNO ₃										
% HNO ₃ in mineral layer	1,24	1,20	1,62	0,84	0,99	0,99	0,99	0,91	1,05	
% HNO ₃ in organic layer										

Under homogeneous and heterogeneous conditions, an increase in the strength of the HNO₃ in a mixed acid results in the reaction velocity rising up to given limits, and then falling (see Table 30 and Fig. 45). Under heterogeneous conditions, the maximum shifts in the direction of mixtures containing more HNO₃. Computation of the strength of the HNO₃ in the mineral layer in terms of the coefficient of distribution shows that its value is the same as that at ^a strength ^{of the} HNO₃ at which the rate of nitration in a homogeneous medium ^{reaches} obtains its maximum.

under

Thus, upon nitration ~~in~~ heterogeneous conditions, reduction of the strength of the HNO_3 in the mineral layer reduces the dinitrotoluene nitration velocity, and the bulk of this chemical is nitrated, apparently, in the mineral layer. As a consequence, as is evident in Table 30, reduction in the velocity of nitration of dinitrotoluene under heterogeneous conditions, as compared to the velocity under homogeneous conditions, is clearly evident when the quantity of HNO_3 is small. Under these conditions, evidently, and thanks to the considerable solution of the nitric acid in ^{the} organic layer, the nitric acid remains in the mineral layer, to only a very small degree. When there is a large excess of nitric acid, no sharp difference in the degree of ~~nitration~~ ^{nitroability} of dinitrotoluene in heterogeneous and homogeneous mediums is observed, as much as, despite its solution in the organic layer, an excess of nitric acid over the amount required for nitration remains in the mineral layer, and therefore high nitroability occurs.



in
Fig. 45 - Effect of HNO_3 ~~on~~ Mixed
upon
Acid ~~on~~ Rate of Nitration of
Dinitrotoluene to Trinitrotoluene
(TNT)

- a) TNT produced, $\frac{g}{litr}$;
b) \circ - homogeneous conditions;
c) Δ - heterogeneous conditions

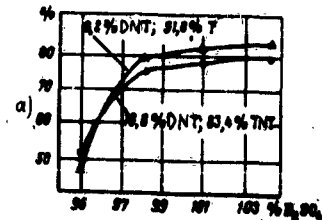


Fig. 46 - Effect of ~~Strength~~ Strength of
Sulfuric Acid upon Rate of Nitration of
Dinitrotoluene (DNT) alloyed with
Trinitrotoluene (TNT)

- a) Amount of DNT nitrated

The maximum rate of nitration at a given concentration of sulfuric acid and a small amount of HNO_3 , such as is observed under homogeneous conditions, is lacking in heterogeneous conditions (see data of Table 31 and Fig. 46, showing the effect of the strength of the sulfuric acid upon nitration ~~velocity~~ velocity (at 100°) of dinitrotoluene alloyed with TNT, when the mixed acids employed contained 10% HNO_3).

Table 31

a)	b)					
	87	91	95	98	101	104
0	7,8	21,0	22,0	—	—	—
24	7,1	19,5	22,0	—	—	—
45	2,0	18,2	22,0	—	—	—
64	0	17,5	27,5	—	—	—
84	0	26,0	48,3	74,0	75,0	78,4
92	—	—	47,0	81,1	82,7	83,9

a) Percentage trinitrotoluene ~~in initial dinitrotoluene~~ in initial dinitrotoluene; b) Dinitrotoluene nitrated in 30 min, in %, at various strengths of H_2SO_4 , %

109

Trinitrotoluene also has a significant effect upon the dinitrotoluene nitration velocity under heterogeneous conditions, although this influence is rather peculiar. Figure 47 shows the influence of TNT upon the dinitrotoluene nitration velocity by mixed acids at 90° . We see that the addition of up to 66 - 70% TNT to the nitrated dinitrotoluene causes a drop of more than 50% in the degree of nitreability. Further increase in the addition results in an increase in the degree of nitreability of the dinitrotoluene which, when the alloy contains 91% TNT, is virtually equal to the degree of nitration of pure

~~XXXXXXXXXX~~

dinitrotoluene.

On the basis of these data, one may conceive of the following reaction mechanism of the nitration of toluene to TNT under heterogeneous conditions.

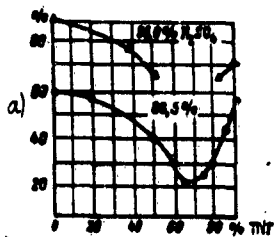


Fig.47 - Effect of Trinitrotoluene (TNT) upon Dinitrotoluene (DNT) Nitration Velocity

a) Amount of DNT nitrated

The nitration of toluene to mononitrotoluene and that of mononitrotoluene to dinitrotoluene under heterogeneous conditions is, to a considerable degree, a "surface" reaction, as is evident from the dependence of its velocity upon the intensity of agitation. The dinitrotoluene nitration reaction under heterogeneous conditions is not limited solely to the interface (as is proved by the low degree of dependence of its velocity upon the intensity of agitation), but penetrates to a considerable depth in the mineral layer (the reaction occurs chiefly in the mineral layer). The reacting components - dinitrotoluene and nitric acid undergo distribution into the respective layers in accordance with their solubility therein and with the ratio of the volumes of layers. In the nitration of dinitrotoluene, the reaction will proceed within both layers. The rate of nitration in the organic layer, which apparently occurs only when the factor of nitrating activity is high, is considerably lower than the rate of nitration in the mineral layer [according to Lewis, by 90% (Bibl.66)].

The reason for this is the fact that the organic layer contains only HNO_3 , inasmuch as H_2SO_4 virtually does not enter this layer. Therefore, if the volume

between the organic and mineral layers in accordance with the solubilities therein, and ratio between the volumes of ~~THESE~~ the layers. As the reaction proceeds and the layer of TNT increases, the quantity of dinitrotoluene dissolved in the nitre mixture diminishes.

The negative effect of TNT upon the nitration velocity is modified somewhat toward the end of the process, when only a small amount of incompletely ~~EXTRACTED~~ nitrated dinitrotoluene remains in the melt. Under these conditions, it is obvious that the relative share of dinitrotoluene in the mineral layer will be greater due to the fact that this layer is not saturated with dinitrotoluene, as a consequence of the small amount of the latter remaining.

Thus, the most favorable conditions for heterogeneous nitration of dinitrotoluene are those existing at the start of the process, when the organic layer consists of pure dinitrotoluene. Under these conditions, the process ~~IS~~ velocity will be maximal.

The least favorable conditions for nitration are those at the end of the process, when the amount of dinitrotoluene active in the mineral layer is small. In order to increase the nitration velocity at the end of the process, it has to be conducted at the higher temperature, or a concentrated acid mixture must be employed. At the start of the process, and as a consequence of the considerable concentration of dinitrotoluene, weak mixed acids may be employed, and nitration may be carried out at lower temperature. Thus, in this process, countercurrent flow between the compound being nitrated, and the mixed acid doing the nitrating is undesirable.

As has already been indicated, the dinitrotoluene nitration reaction in heterogeneous conditions proceeds primarily in the mineral layer, and consequently, its velocity is determined by the volume of this layer, and the concentration of the reacting components therein. These latter may be determined on the basis of the coefficient of distribution of these components between the mineral and organic layers.

In World War II, nitration of toluene to TNT was performed in three stages, in the majority of the warring countries, with complete acid circulation. ~~XXXX~~ The third stage employed a mixed acid made of fresh acids; whereas the second and first ~~XX~~ stages made use of mixed acids prepared from the spent acid of the preceding stage of nitration, and nitric acid. As a rule, the process was run in batch-type apparatus. Processes of this type were employed in the USA (Bibl.67, 68), Germany (Bibl.58, 67, 68), and Japan (Bibl.67).

In England, TNT was produced by nitration of toluene by the so-called countercurrent method. The first stage - nitration of toluene to mononitrotoluene - was carried out in ordinary batch-type nitrators. The second and third stages - the nitration of mononitrotoluene to TNT - were performed in continuous-acting apparatus of special design, which divided this process into 14 sub-stages (Bibl.20). This "countercurrent" method of nitration makes for the most economical utilization of sulfuric and nitric acid.

In the three-stage method of producing TNT, the consumption of acids is considerably greater than in the "countercurrent" method, and this makes it less advantageous from the economic point of view. However, this method also has

positive aspects, to wit: a) compactness of the nitration units, and b) the fact that the raw TNT obtained has a high freezing point (79.5 - 79.6°), and virtually requires no further purification. The purity of the TNT obtained is explained by the fact that, in this situation, nitration is performed at a lower temperature, and with concentrated mixed acids. Together, these facts lead to a reduction in the meta-isomer content, and subsequently of the asymmetrical ~~XXXXX~~ trinitrotoluenes contaminating the TNT.

German methods of TNT production. Coal and synthetic toluenes were employed in Germany during World War II for TNT manufacture.

Synthetic toluene (made from benzene and methanol) did not differ in quality from that obtained from coal, and was employed under ^{identical} ~~identical~~ production conditions. The major specification to be met by the toluene was the distillation interval. Not less than 90% of the toluene had to go over in a range of 0.6°, and not less than 95% in a range of 0.8°.

At some plants, mononitrotoluene, containing about 1% meta-isomer was used as the starting substance. This mononitrotoluene was provided by ~~XX~~ ~~XXXXXXXXXX~~ I.G. Farbenindustrie, which isolated meta-nitrotoluene for dye production from technical mononitrotoluene ~~XXXXX~~ (Bibl.5, 70).

Figure 48 illustrates the flow sheet for nitration of toluene to TNT.

The mononitrotoluene was produced in the semi-continuous apparatus (Bibl.70). The process consisted of preliminary nitration in a continuous apparatus (pre-nitrator) and completion of the nitration in a batch-type apparatus.

¹Toluene and mixed acid prepared from fresh acid, and consisting of 60% H_2SO_4

25 - 28% HNO_3 and 12 - 15% H_2O , are delivered to the ~~XXXXXXXXXX~~ ^{pre-nitrator} through variable-area flow meters. The temperature of nitration is 36 - 38°. The pre-nitrator is a tubular heat exchanger with an interior impeller making 360 rpm. The contents of the pre-nitrator proceed continually to a second batch-type nitrator, where nitration of the process is completed in about 4 hrs.

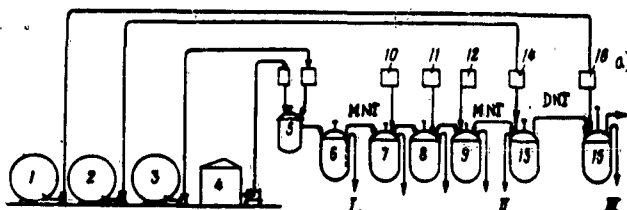


Fig.48 - Flow Sheet Showing Process of Nitrating Toluene to TNT

1 - Storage for third-stage mixed acid; 2 - Storage for second-stage mixed acid; 3 - Storage for first-stage ~~MX~~ mixed acid; 4 - Toluene storage; 5 - Preliminary ~~XXXXXXXXXX~~ nitrator; 6 - First-stage nitrator; 7, 8, 9 - Apparatus for washing mononitrotoluene; 10 - Water tank; 11 - Soda solution tank; 12 - Tank ~~MX~~ for ~~MX~~ NaOH solution; 13 - Second-stage nitrator; 14 - ~~XXXXXXXXXX~~ ^{Metering} device for second-stage mixed acids; 15 - Third-stage nitrator; 16 - Metering for third-stage mixed acid
a - TNT to washing

After the batch-type nitrator has been filled with the product, delivery from the ~~XXXXXXXXXX~~ ^{pre-nitrator} is switched to a second batch-type nitrator analogous to the first, and the first then switches to separation of/mononitrotoluene from the spent acid ~~XXXX~~ by settling.

The spent ~~MX~~ acid then goes to recovery. Acid containing less than 0.3% nitric acid is sent immediately to concentration, without denitration.

After separation from the spent acid, the mononitrotoluene is washed with water, neutralized with soda, and cleaned by live steam distillation. These operations are held to be necessary if unpurified toluene is employed in nitration. The fraction containing ~~gasoline~~ and incompletely nitrated toluene, which are removed by steam distillation, is 3 - 4%.

112 Some plants in Germany have installations for ~~vacuum distillation~~ of the mononitrotoluene so as to separate the meta-isomer. It was assumed that this would make it possible to eliminate subsequent purification of the TNT. However, operating experience at these plants showed that separation of a meta-isomer presented major engineering difficulties, and that it was very difficult to obtain mono TNT virtually free from meta-isomer.

The production of the dinitrotoluene is carried out in another building in batch-type nitrators (the nitrators were of 15 m³ capacity). The mixed acid used in this stage was spent acid from the third stage with the addition of nitric acid. At a number of enterprises, the mixed acid was made in the nitrator, with mononitrotoluene then run in. Nitration temperature was 55 - 80°.

The dinitrotoluene obtained was separated from the spent acid ~~in~~ in the fused state. Separation was performed directly in the nitrators. The spent, separated acid, was forced into special containers by compressed air, and the dinitrotoluene was then delivered by pressure into the third-stage nitrators.

The spent acid was diluted with water to obtain ~~73 - 75%~~ 73 - 75% H₂SO₄, the residual dinitrotoluene being extracted ~~there from~~ there from at 40° in the course of an hour, subsequent to which the spent acid was sent ~~for~~ for regeneration. The

mononitrotoluene employed for extraction is nitrated to dinitrotoluene.

The TNT was obtained by nitrating the dinitrotoluene, also by a batch-type method. Nitration ~~employed~~ employed mixed acid of the following composition: 80% H_2SO_4 and 20% HNO_3 . The process was conducted by running dinitrotoluene into the mixed acid at 72 - 76°, followed ^{by} a slow raising of the temperature to 96°, and holding at that temperature for 2 - 2.5 hrs. The resultant TNT was separated from the spent acid after slight dilution of the spent acid with water (to bring ^{the} water content up to about 10%). The spent acid, containing about 10% nitric acid and nitrogen oxides was employed to produce dinitrotoluene.

All three stages of nitration have their own absorption equipment to trap the nitrogen oxide and the nitric acid fumes. The apparatus also ~~provided~~ provided for complete absorption of toxic gases, with the consequence that grass, brush, and trees planted around these enterprises did not suffer in the slightest.

A number of German plants had experimental apparatus for continuous nitration of toluene by the so-called direct-flow and countercurrent methods.

The direct-flow single-stage method of nitration. The mixed acid nitrates toluene vapors to TNT in a single stage in the following manner.

The toluene is pumped from storage to a vaporizer, where it is heated and a current of air or nitrogen is passed through it to entrain the toluene vapors in the nitrator. The ~~nitrator~~ ^{nitrator} (Fig.49) is a broad vertical tube surrounded by another tube constituting the separator. The nitrator is filled with mixed acid. Its lower portion contains a perforated bottom. The mixed acid and mixture of air and toluene are run in beneath this bottom, and then pass in thin streams through the column of acid. The toluene is nitrated to TNT at 90 - 95°. Cells

within the tube serve to remove the heat of reaction. The process of nitration is regulated by the toluene delivery and this in turn is regulated in accordance with temperature readings.

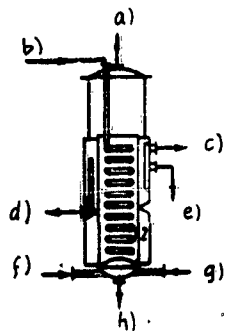


Fig.49 - Continuous-Flow Nitrator

1 - Nitration portion; 2 - Separation portion

- a) Flue gases; b) Water to coil;
- c) Acid drainage; d) TNT; e) Acid circulation; f) Mixed acid; XX
- g) Vapors of toluene and nitrogen;
- h) Dump to emergency tank

Half of the spent acid and TNT are removed from the separator. Addition of oleum and nitric acid to the spent acid remaining in the apparatus is employed to make fresh mixed acid, which

is recycled for nitration. The spent acid that has been separated off is diluted with water. The dilute TNT thus separated is extracted, and the acid is sent to concentration. The mixed acid is 10% in total acidity (consisting of

40 - 60% oleum and strong nitric acid). The raw TNT produced has a freezing point of 78°.

A shortcoming of this method is the large quantity of spent acid. To eliminate this shortcoming, it was suggested that nitration be performed in two stages: toluene to mononitrotoluene, and mononitrotoluene to trinitrotoluene (so that a portion of the spent acid ^{from} the second stage be employed in the first stage).

Direct-flow two-stage method of nitration (Bibl.58). This process consists of the following stages: first stage nitration and separation, second stage nitration and crystallization of TNT from the spent acid, centrifuging, washing with water

(without sulfite), air drying, filtering through thin flannel, and flaking.

First-stage nitration is performed in four nitrators connected in series, and constituting a column containing a screw-type agitator making 200 rpm. Plates to intensify the stirring are seated on the nitrator walls. The toluene and mixed acid of the following composition: 68% H_2SO_4 , 17.5% HNO_3 and 14.5% H_2O , are delivered into the first nitrator from above metering devices. The worm impellers deliver the components through the nitrators connected ⁱⁿ series in a direction opposite to their tendency to separate into layers. The nitrators are provided with jackets for cooling with water or heating with steam, and coils are lacking, as there would be no room for them within the column. Nitration is performed at 30° , with the object of reducing the yield of meta-isomers.

As a result of the first nitration, a mixture of nitrotoluene and dinitrotoluene is formed. The nitro product is ~~EX~~ separated from the spent acid in a separator shaped like a U-tube. The spent acid, having the following composition, 70% H_2SO_4 , 6% HNO_3 , and 24% H_2O , goes to denitration after settling. The liquid nitro product (specific gravity 1.3) goes to second-stage nitration to TNT, which is performed in six nitrators. The temperature in these nitrators is held within limits of 70 to 115° . The nitro mixture is of the composition: 86% H_2SO_4 and 17.5% HNO_3 , i.e., it ~~contains~~ ^{contains} free SO_3 .

As distinct from the methods employed in Germany, TNT obtained by the two-stage method, is not separated from the spent acid in a liquid condition, but the nitro mass is sent to containers in which crystallisation of the TNT out of the acid occurs upon stirring (70 rpm) and cooling. From these containers, the

batch goes to centrifuges, where the acid is removed, and washed with water.

Dilution of the spent acid with water is employed to ~~separate~~ ^{separate} out the dissolved nitro product, which is utilized to obtain industrial explosives, whereas the spent acid goes to first-stage nitration to make mixed acid.

Thus, purification of TNT consists of slow crystallization of the raw TNT, in which the crystals of the α -isomer are separated out in the pure state, and impurities are distributed over the surface of crystals, from which they are readily removed by washing in water. After purification, the TNT is fused and dried by blowing compressed air through it. This compressed air is continually delivered ~~into~~ into the drying bath. The TNT is then filtered through a flannel filter and flaked with a drum. The resultant product is characterized by high purity, is of an absolutely white color, and its freezing point is 80.7° . The toluene consumption per ton of raw TNT is 0.465 ton, whereas per ton of purified TNT, it is 0.506 ton.

"Countercurrent" nitration (Bibl.71). Figure 50 shows an installation for "countercurrent" nitration of dinitrotoluene to trinitrotoluene.

The dinitrotoluene goes to the No.1 apparatus, where it is mixed with the mixed acid from apparatus No.2, where it was utilized virtually in full. The batch then goes to separation tube b, from which the separated nitro product is sent to apparatus No.2, where it is immediately mixed with the somewhat stronger acid arising from apparatus No.3.

In apparatus No.1, the spent acid is separated, beneath the perforated plate a, from the nitro product, and is removed from the apparatus by means of separation

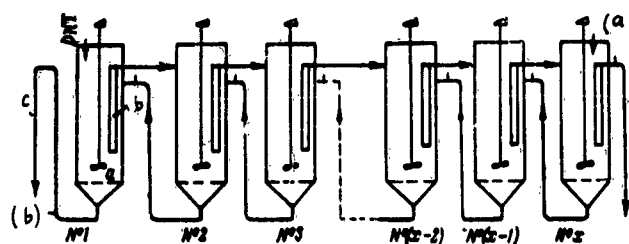


Fig.50 - Countercurrent Nitration of Dinitrotoluene (DNT)

From No.1 through No.x - combination equipment; a - Perforated plate; b - Separation tube; c - Siphon

(a) Acid; (b) Spent acid

tube c. The nitrating mixture goes to apparatus No.x, where it is mixed with the almost completely nitrated dinitrotoluene arising from apparatus No.(x - 1). The TNT is removed from apparatus No.x while the slightly-diluted mixed acid, separated from the TNT below the perforated plates, is sent via the ~~XXXXXX~~ ^{siphon} tube to apparatus No.(x - 1) countercurrent to the somewhat less nitrated product.

Methods of producing TNT in USA (Bibl.20, 67, 68, 72). In the USA, during World War II, TNT was produced in three stages, as in Germany. The difference between the American and German methods lies in the fact that in the USA, the mononitrotoluene goes directly from the first stage of the nitration to the second, and is not subject to any further operations. The mixed acid for nitrating toluene to mononitrotoluene is of the following composition: 48% H_2SO_4 ; 18% $HMSO_5$; 14% HNO_3 ; 8% nitre products; 12% H_2O .

This mixture is prepared by mixing the spent acid (from the second stage of nitration) with fresh nitric acid. After the first stage, a portion of the spent

acid is poured into a nitrator. Toluene is run in, and it is only then that mixed acid is gradually added. In the presence of the first mixed acid as medium, the reaction goes more smoothly.

115 After the ~~first~~ completion of nitration, the mononitrotoluene is separated from the spent acid and sent to the second stage. A portion of the spent acid is employed for nitration of the next charge of toluene, and the remainder is subjected to the nitration with subsequent concentration to 98% sulfuric acid. This last is employed in the production of oleum.

The spent acid from the third-stage ~~nitration~~ nitration is mixed with nitric acid and sent to the second stage. This mixed acid is of approximately the following composition: 50% H_2SO_4 , 20% HNO_3 ; 12% $HNSO_5$; 12% nitro products, and 6% H_2O .

The fresh mixed acid employed for the third stage is made of spent acid from the third stage, to which one first adds 30 - 40% oleum (containing 60% SO_3), and then a mixture of 40% H_2SO_4 and 60% HNO_3 .

Improvement of TNT production has chiefly followed the line of increasing the yield of the apparatus by reducing cycle time (Bibl.68). Thus, at the Plumb Brook Plant in Ohio, the production cycle for making 1.5 ton of finished ~~TNT~~ product initially ran 2 hrs 10 min. When the plant operated ~~in~~^{on} three shifts, this made possible the production of about 16.5 tons of TNT per day on a single line. Toward the end of the war, the length of a cycle at this plant was reduced to 60 min, which made it possible to bring production to 53.5 tons per day on the line, excluding loss of time due to mechanical difficulties.

this increased production

As pointed ~~out~~ by Raifan~~ider~~ (Bibl.68), [^] was achieved by reducing the production cycle to 1.5 hours through shortening the excessively lengthy periods assigned to cooling, settling, and separation. ~~Simultaneously~~ Simultaneously, both the ^{the} process itself and/equipment were modified.

Under the method employed, nitro mixture was gradually added to the complete dinitrotoluene charge. The addition was performed in two stages. First, the entire amount of oleum required was slowly added, and then a third of the mixture (50% H_2SO_4 and 50% HNO_3) ^{was} ~~was~~ added thereto. At the beginning of the run-in of the mixture, the apparatus contents foamed (due to the emission of a considerable amount of heat). Foaming made it difficult to adjust temperature and, not infrequently, the foam ran through the apparatus, giving rise to the possibility ^{and} of fire/explosion. To ~~EX~~ avoid these phenomena, the sequence of component run-in was changed. The product subject to nitration came to be added to the entire amount of acid charged, with intensive agitation. As a consequence, the amount of material to be nitrated in the nitrator was quite small as compared to the mixed acid.

In the first and second stages of nitration, the product was almost entirely nitrated by the end of the run-in. In the third stage, after the dinitrotoluene was run in, although it was still necessary to hold it for some period, this method eliminated the danger of foaming and substantially reduced the overall nitration ^{time} ~~plan~~. Temperature was regulated more evenly, as the product being delivered was immediately nitrated virtually to completion. Regulation of the delivery of the product to be nitrated maintained the required temperature and process time was reduced to the minimum required. Pyrex glass tubes, permitting

ready observation of the interface between nitro ~~XXXXX~~ product and acid were installed on the separation ~~XXXXX~~ lines.

Methods of TNT production in England (Bibl.20, 73). During the Second World War, TNT was produced by the two-stage method at the majority of British plants. The first stage yielded mononitrotoluene, and the second TNT, by countercurrent nitration of the mononitrotoluene. The first installation for countercurrent nitration was in operation in England as early as World War I. During the Second World War, and possibly somewhat earlier, major British scientists performed significant studies of the process of nitration of dinitrotoluene to TNT (Bibl.63, 64). This doubtless played an important role in the development of a method of TNT production more advanced than that of Germany and the USA, countercurrent nitration being basic thereto.

In the first stage, nitration of toluene to mononitrotoluene is carried out in the usual cast iron batch-type nitrators. Nitration is performed by running the toluene into the mixed acid in the nitrator. This mixed acid is prepared from spent acid (from the second stage) and weak nitric acid. During the run-in of the toluene, the temperature of the nitro mass in the nitrator gradually rises from 15° to 35°, and it then held at that temperature for 20 min. Upon completion of nitration, the content of the nitrator is transferred by compressed air to a separator in the form of a column. A spent acid (from the first stage) goes to denitration. The resultant mononitrotoluene contains about 6% dinitrotoluene (of the spent acid of the second stage) and should not contain toluene ~~XXXXX~~ (this is one of the required conditions for safety in stage 2).

When toluene with elevated ~~gasoline~~ gasoline content is nitrated, the first-stage product is subjected to distillation. ~~Removal~~ Removal of the gasolines reduces the consumption of nitric acid in nitration, and also eliminates the possibility of ignition during the second stage.

The supplementary operation of distillation does not increase the cost of TNT, as TNT containing gasoline is considerably cheaper than pure TNT.

The second stage is carried out in a unit consisting of 14 nitrators and 14 separators. The separators are installed higher than the nitrators. The nitrators are cylindrical ~~IX~~ vessels provided with agitators and coils for delivery of water or steam thereto, with the purpose of regulating the temperature of the nitro mass. The separators also consist of cylindrical vessels of the same diameter ^{the} as nitrators, but of only one-half the height. The interior of the separators follows the pattern of a Florentine receiver.

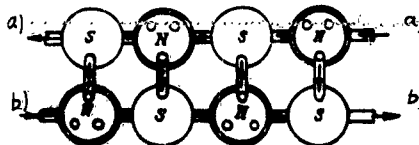


Fig.51 - Diagram of Countercurrent Nitration of Toluene. N - Nitrator;
S - Separator
a) Nitro product; b) Acid

From the nitrator, the nitro ~~IX~~ mass is delivered to the separator by means of an Archimedes-screw. The separated components flow through ^{troughs} ~~troughs~~ from the separator into the respective nitrators, by gravity. The nitrators

and separators have holes in their bottoms (covered by lead disks), through which they connect to emergency containers by pipe.

Figure 51 shows a planned view of the nitrator and separator arrangement.

The process takes the form of charging mononitrotoluene into the first nitrator. When it is passed in sequence from the first nitrator to the separator, the second nitrator and the second separator, etc. through the fourteenth separator, it emerges in the form of TNT. 96% sulfuric acid is run into the fourteenth nitrator, and follows a course counter to that of the oil, emerging from the first separator as spent acid. Strong nitric acid is run into the middle nitrators.

The temperature in the separators has to be the same as in the nitrators.

Extraction of nitric acid from the spent acid by mononitrotoluene is performed in the first nitrator. Water is introduced into the second nitrator to ready the spent acid for the ~~EX~~ first stage. Moreover, the water, diluting the spent acid, diminishes the solubility of mononitrotoluene therein.

Table 32 shows the conditions under which the apparatus operates.

The process is monitored by determining the ~~EX~~ freezing point of intermediate and final nitration product. The freezing points of the nitro products emerging from nitrators Nos. 5, 6, 7 and 14, are determined. The freezing point of the nitro product from apparatus Nos. 5, 6, and 7 must diminish with increase in apparatus number, and this testifies to increase in TNT ~~XXXXXXXX~~ content. To avoid spoilage, the amount of mononitrotoluene added is reduced.

Table 32

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
a)														
b)	40	40	70	100	100	100	100	100	100	100	100	100	100	90
c)	d)	e)	f)											g)
h)	i)		15	35	50	45	41	35	55	63	69	72	76	77

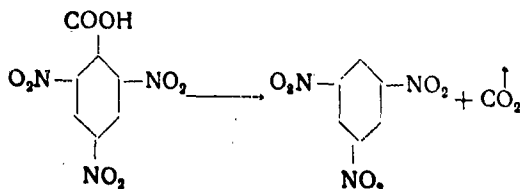
a) Apparatus number; b) Temperature, °C; c) Run-in of components; d) Mononitrotoluene; e) Water; f) Strong nitric acid; g) 96% H₂SO₄; h) Freezing point of nitro product, in °C; i) Liquid product freezes at considerably below 15°

118 b) Washing Acid Out of the TNT

The TNT produced in the nitration shop contains 3 - 5% acid, which has to be removed. The acid added to the TNT as a consequence of the complete separation, as well as that dissolved therein, is removed by washing with water. The use of caustic to neutralize acid in the final washing is not permitted, as a consequence of the possibility that highly-sensitive metallic TNT derivatives of low stability may result.

TNT is washed with hot water, usually in the molten state. When this is done, it is not only the mineral acid, but a portion of the side reaction products, ~~especially~~ such as trinitrocresol and trinitrobenzoic acid that go into solution.

Upon hot washing, the latter converts in part to trinitrobenzene:



In Germany, the washing of TNT was performed by mixing the fused products with the wash liquid and subsequent decantation in the same apparatus. The washing apparatus is of the same design as the nitrators. The residual wash liquid is evacuated by compressed air. The TNT is washed thrice: with water, with 3 - 4% soda solution, and again with water.

In the USA and England, TNT is washed in tanks with stirrers, hot water alone being used. This is done 4 - 6 times until residual acidity is 0.01%. The loss

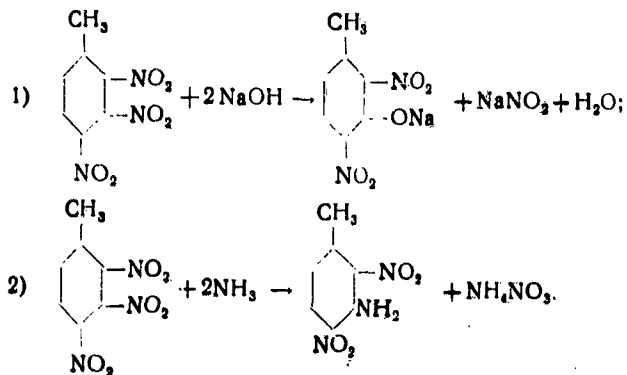
~~XXXXXXXX~~

usually
of TNT in the wash water ~~XXXX~~ reaches 0.5%.

c) Purification of the TNT

The washed TNT (raw), having a freezing point of not less than 77.4°, contains up to 6% impurities, consisting chiefly of asymmetrical isomers of TNT and dinitrotoluene, as well of tetranitromethane, oxidation products, etc. The impurities induced production in the ~~XXXX~~ freezing point of TNT and diminish its service characteristics (causing it to be oily). ~~XXXX~~ Therefore, the raw TNT is subsequently purified of these admixtures either by chemical means (converting the impurities into water-soluble compounds) or by a physical means (crystallization out of the solvents or washing the crystalline TNT with solvents).

Chemical method of purification. This method of purification of raw TNT is based upon conversion of the impurities by reacting them with a reactant in the water-soluble compounds. It is not difficult to choose such reactants, as the major impurities of asymmetrical trinitrotoluenes which readily substitute for the nitro group in the meta-position with respect to methyl group. Reactants of this type may include caustic, ammonia, methylamine, and other ^{amino} ~~XXXX~~ derivatives, reacting with asymmetrical trinitrotoluenes in accordance with the following mechanisms (Bibl.74):



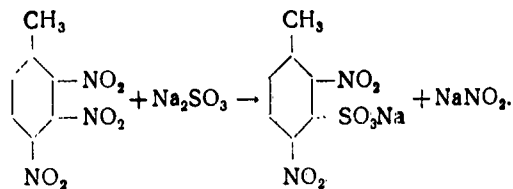
The ~~XXXXXXXXXX~~ dinitrotoluidine obtained by the second of these mechanisms goes into solution in the form of sulphate salts when treated with sulfuric acid.

Sodium sulfite proved to be a more convenient reactant, and in the course of the last 30 years it has been widely employed for the purification of raw TNT.

Sulfite purification is based on the fact that sodium sulfite reacting with the majority of the impurities obtained as a ~~XXXXXXXXXX~~ consequence of side reactions and nitration of the impurities in the toluene forms compounds soluble in water and in ^{aqueous} ~~XXXXXXXXXX~~ sodium sulfite solution, with the ~~XXXXX~~ result that the impurities are readily washed out in subsequent ~~XXXXXXXXXX~~ operations.

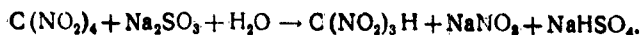
The effect of aqueous solutions of sodium sulfite upon the impurities varies.

Sodium sulfite reacts in the cold with asymmetrical isomers of trinitrotoluene to form sodium ~~XXXXX~~ dinitrotoluene sulfonates, which are ^{readily} ~~XXXXX~~ soluble in water:



In the opinions of certain observers, the replacement of the nitro group by the sulfo group is an oxidation-reduction reaction. In this process, the nitrogen of the nitro group is reduced to the trivalent form ^{(the nitro} ~~XXXXX~~ /group is removed from the ring in the form of the nitrous salt), and the sulfur of the sulfite group undergoes oxidation to hexavalence, and enters the ring in the form of the sulfo group.

Tetranitroethane reacts with comparative ease with sodium sulfite. The end product ~~XXXX~~ is trinitromethane - a substance that is readily soluble in water, and produces a yellow color:



With trinitrobenzene, an addition compound, bright red in color, and ~~XX~~ readily soluble in dilute ~~XX~~ sodium sulfite solution is formed.

The phenol type oxidation products are also readily soluble in dilute solutions of sulfite, and form phenolites.

Dilute sodium sulfite solutions do not act upon incompletely nitrated impurities in TNT, such as dinitrotoluene, dinitrobenzene, and also on trinitrometaxylene. Therefore, TNT going to sulfite purification has to contain at least some minimum of these compounds.

At low temperatures, dilute sodium sulfate solutions do not act upon α -isomer, but in stronger concentrations, they form additive and other compounds of α -trinitrotoluene and sodium sulfite, which give the solution a bright red color.

Some ~~XXXX~~ are ~~XXXX~~ of these compounds/decomposed by water with consequent recovery of α -trinitrotoluene. The solubility of α -trinitrotoluene in sodium sulfite solutions depends upon the strength of the solution, as is evident from the following data:

dissolves
3% sodium sulfite solution ~~XXXXXX~~ 0.3% α -trinitrotoluene at 20°; 6% sodium sulfite solution dissolves 0.6% α -trinitrotoluene at 20°; 12% sodium sulfite solution dissolves 2.3% ~~XXXXXXXX~~ α -trinitrotoluene at 20°.

Consequently, even a 6% solution is a solvent of sufficient strength, to cause considerable TNT losses.

Thus, when 250 cc of 5% Na_2SO_3 solution acts upon α -trinitrotoluene at 30, 40, 50 and 60°, the total losses are 0.9, 1.1, 2.0, and 5.0 gms, and the irreversible losses are 0.4, 0.6, 1.5 and 5.0 gms respectively.

Consequently, losses of α -isomer increase considerably as temperature ~~is~~ is raised over 40°. Moreover, the losses become irreversible, as the solution is diluted, and this indicates that the resultant compounds are of different character. Minimum loss of α -TNT occurs when it is treated with sulfite for a maximum of 1 hr at a temperature of less than 40°, and is diluted with an equal quantity of water ~~immediately~~ immediately at the end of the reaction. ~~Therefore~~ Therefore, the effect of the strength of the sulfite solution and the process temperature are taken into consideration, and dilute solutions are employed in industry, ranging in strength from 2 - 5% of active sulfite, and the treatment is performed usually at temperatures of less than 60°. When more dilute sodium sulfite solutions are used, (approximately 2%), purification may be conducted even at 75°. Under those circumstances, the losses of α -isomer are comparatively small.

Treatment with sulfite solution yields the best results if it is conducted with TNT in crystalline form, or, at least, in the form of finely crushed grains. Inasmuch as, in the process of crystallization, liquid impurities gather on the surface of these crystals as a thin film, they are readily subject to the effect of the sulfite, whereas in dilute TNT or in large grains, the impurities are distributed throughout the mass and are, as it were, protected against the effects of the sulfite. For this reason, the washing of TNT in the United States and Germany (Bibl. 20, 67, 68) is preceded by crystallization of the fused TNT under water.

The major apparatus in the sulfite purification shop consists of crystallizers and funnels.

A crystallizer is a vertical welded chromium-nickel cylindrical tank covered by a layer of insulating material on the outside. Inside the crystallizer, is a frame-type agitator rotating at 25 rpm. Rotation of the stirrer is by means of an electric motor housed in a closed space above the crystallizer or outside a structural wall.

Steam, water from a heater, and product lines from the TNT metering device and the sulfite solution metering device are led into the crystallizer. For removal of the steam and to ~~cool~~ ^{cool} the crystallizer contents (by forced air intake), ventilators are attached to the roof. An unloading flange, with valve, are provided in the bottom of the crystallizer.

The funnel is a cast iron or welded-chromium nickel-cylindrical vessel with a conical bottom. The lower portion of the cylinder is a lattice work over which is placed the filtering grid and a sheet of aluminum with holes to protect the filter from destruction during the unloading process.

121

Hot water ~~IX~~ from a heater is ~~IX~~ fed to the funnel. The water mains are in the form of tubular rings with openings (sprinkler rings). At the bottom of the casing there is a drain for the sulfite and wash waters. At the middle of the casing, (directly below the mesh carrying the filtering fabric) is a TNT ~~XXXXXXXX~~ drain. After washing out the impurities, the TNT is melted by the delivery of live steam through annular ~~bubblers~~ ^{bubblers} placed above and below the false bottom.

The funnel serves to remove and wash out the sulfite solution and the impurities dissolved therein, which form as a consequence of the treatment of TNT

by sodium sulfite. Hot water is also employed to wash the ~~XXXXXXXX~~ ^{fusible} TNT impurities that are precipitated on the surface of the crystals during crystallization (dinitrotoluene, dinitrobenzene).

With the stirrer in operation, hot water (at a temperature of not less than 80°C) and fused TNT (the ratio being 1:1 by volume) are run into the crystallizer. The fans are operated to cool the mix. When the temperature in the crystallizer reaches 56 - 58°, the sodium sulfite solution is run in (in the form of 10 - 15% solution). In the United States, 16% sulfite solution, containing 0.5% bisulfite is employed.

The impurities are ^{separated} ~~XXXXXXXX~~ out of the TNT during crystallization. They undergo distribution on the surface of the crystals of pure α -isomer and therefore become more readily accessible to the effect of the sulfite. If the regularity of crystallization is interfered with by sudden cooling or nonuniform stirring at various times of crystallization, crystal concretions or granules may ~~XXXX~~ be formed. Within these ~~XXXXXXXXXXXXXXXXXXXX~~ concretions and granules, the TNT crystals will be inaccessible to washing with sulfite solution. This reduces the quality of the TNT and results in the production of a low-quality product. Even ^{best} if, in the ~~XXXX~~ instance, the granules form after the sulfite acts upon the impurity, they may still be the cause of the production of ^a ~~the~~ product of poor quality, as they will contain the mother ^{liquor} ~~solution~~ of sulfite, which will not yield to washing by water on the funnel.

~~XXXX~~ It must be observed that the crystallizer has to have a motor of sufficient power so that, if the agitator stops accidentally during crystallization,

It will be able to be restarted.

TNT from the crystalliser is emptied into the funnel, along with sulfite solution. In order for this unloading to be uniform, the crystalliser agitator continues to operate until the apparatus has been entirely emptied, and the valve through which the mass is emitted is periodically cleansed with a copper rod.

The sulfite mother liquor is taken off by suction at the funnel into a special receiver. The TNT is then washed repeatedly with water. The temperature of the wash water has to be in the range of 60 - 68°C. Hotter water may fuse the TNT crystals into lumps, while colder water will not melt the dinitrotoluene impurity remaining on the surface of the crystals as a film. Both result in unacceptable ~~products~~ products, as in the first instance, the lumps will contain sodium sulfite mother ~~liquor~~ liquor, and in the second, the TNT will not have been freed from dinitro ~~derivatives~~ derivatives.

The TNT crystals are washed on the funnel until clear wash water is obtained (absence of fused dinitrotoluene), and until a satisfactory analysis for absence of sodium sulfite is obtained. The freezing point of the TNT must ~~not~~ not be less than 80.3°C.

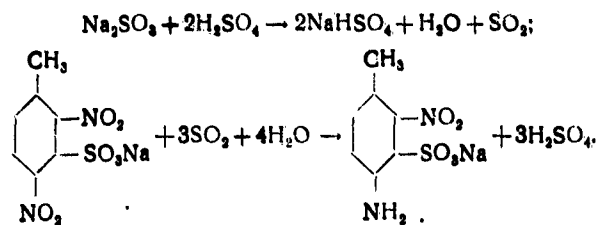
TNT for analysis is ~~sampled~~ ^{tapped} from the funnel (at its middle, ~~in terms of~~ in terms of height), and the wash water is discharged through a drain line.

The spent ~~sodium sulfite~~ sodium sulfite and the washed alkaline water must not be sent into the same trap as the acid wash water (two catch boxes should be provided, one for caustic and the other for acid water), for the following reasons. Sulfite

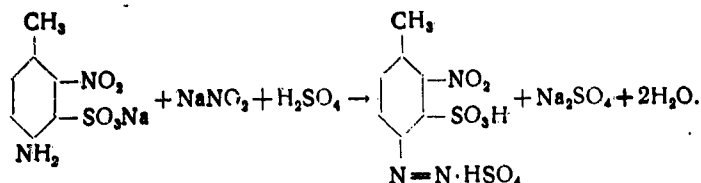
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water contains sodium salt, and dinitrotoluene contains sulfite acids

$\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_2\text{SO}_3\text{Na}$, sodium sulfite Na_2SO_3 and sodium nitrite NaNO_2 . When this water mixes with acid water containing H_2SO_4 , the following reactions may occur, as demonstrated by Battagay (Bibl.62);



The sodium salt of the nitro amino toluene sulfuric acid will undergo diazotization in an acid medium:



The end product of the reaction will be nitrodiazotoluene sulfuric acid, which is unstable to the effect of temperature and exceedingly sensitive to shock, as a consequence of which its formation is dangerous and undesirable.

A major advantage of the sulfite purification of TNT is the simplicity of the equipment involved. The bulk of the apparatus is readily replaceable and inexpensive.

Sulfite purification of TNT is a less dangerous operation (particularly with respect to fire) than crystallization ~~XXI~~ out of the solvent. However, a

considerable accumulation of TNT in the apparatus sharply reduces this advantage, chiefly because of the fact that they function batchwise. Let us remark in passing that the intermittent nature of the process renders automatic monitoring and control virtually impossible.

Sulfite purification of the crystallized TNT, and particularly, the process of crystallization of TNT under water in continuous apparatus presents major difficulties. The problem of sulfite purification by ^{the}continuous method is readily solved, if it is to be performed with fused TNT. However, this method has significant disadvantages, when compared with purification of the crystalline product, the most important of these ^{disadvantages} ~~disadvantages~~ being the lower degree of purification and the increased losses of α -isomer due to the ~~the~~ high temperature at which the purification proceeds.

In purifying fused TNT, fine emulsification is required to increase the contact surface between the reacting components. Under these conditions, the freezing point of the raw TNT may be raised by a 2 - 2.2°.

In Germany, the sulfite purification of TNT in the melted state was performed under the following conditions: 6% ~~sulfite~~ sulfite solution, which was from $\frac{1}{4}$ to $\frac{2}{5}$ of the TNT by weight, temperature 80°C, sulfite solution treatment time 15 - 20 min. Another variant saw the purification performed at 80 - 82° by a 1% sodium sulfite solution equal in weight to the TNT being purified. After the sulfite purification, the TNT was washed two or three times with water and then sent to drying.

123

In England, the TNT was purified only in the melted condition. Purification

was conducted in containers having stirrers in which the TNT had previously been washed free of acid. A 1.5% sodium sulfite solution (1 part solution by weight to 1 part TNT by weight) was added to the fused TNT at 75 - 77°, and stirred for an hour. Two such washings were performed. When high quality TNT was to be made, a 2% sulfite solution was prepared for the sulfite washing.

At the end of the war, sodium sulfite was replaced in the United States by ammonium sulfite. The TNT was purified without prior washing. This measure significantly increased the yield of product and at the same time substantially reduced the overall purification cycle (Bibl.68).

Physical methods of purification. The sulfite method of purification of TNT has very significant shortcomings: large irreversible losses of product (up to 10%) and the formation of a substantial quantity of very ~~toxic~~ toxic spent water. Physical methods of purification of TNT, based upon recrystallizing it out of solution or upon washing the crystals with solvents, reduce the irreversible losses. The ~~IX~~ impurities separated out of the solvent may be employed as explosives.

recrystallization

In Germany, ~~recrystallization~~ of TNT from alcohol, from toluene, and from nitric acid, was employed.

Recrystallization of TNT from alcohol is one of the longest-known methods of purification. The TNT was first ~~be~~ washed to proper acidity.

In Germany, when crystallization from alcohol was performed, the alcohol to TNT ratio was 3:1 i.e., the product was not completely dissolved, but was merely washed with hot alcohol, and crystallized in the presence of alcohol. The TNT was separated from the mother liquor in a vacuum filter and washed with pure alcohol taken in ~~IX~~ 1:1 ratio.

on the
At one plant, the drying of TNT was performed ~~with~~ vacuum filter ~~which~~ which was used for separation of the mother alcohol and washing with pure alcohol. The suction air was passed through a regeneration apparatus. After separation of the mother and wash alcohol, hot air (temperature 60°C) was ~~also~~ directed beneath the filter mesh. The product on the filter was stirred with an agitator. The air passed through the mesh and layer ~~of~~ of products. When the filter diameter was 3 m and the charge was 300 - 400 kg of TNT, drying ~~time~~ took about 4 hrs. This method of separating the mother liquor ~~and~~ and of drying the product made it possible to reduce alcohol losses to 2%.

Alcohol employed in purification may be used 5 - 6 times subsequent to which it is sent for redistillation. The consequence is ~~the~~ repurified alcohol and an admixture of TNT, which, under the title of "trotyl oil" is employed in the manufacture of ammonites. Alcohol purification of TNT offers only two advantages: the absence of toxic wash waters and the possibility of making use of the impurities separated from the TNT. However, this method has a number of significant inadequacies. The most important of these are the losses of costly solvent, the bulkiness of the apparatus, the danger of fire and of explosion, and certain other shortcomings as well. In Germany, crystallization of TNT from toluyl was apparently carried out in accordance with the same technology as crystallization out of alcohol. The difference lay in the fact that the TNT was completely dissolved in the toluene at 60°C. To do this, one part toluene by weight ~~was~~ was employed ~~per~~ ^{per} 0.9 part TNT. The solution was cooled to 25°C, and the TNT ~~that~~ that crystallized out was centrifuged, and then washed repeatedly. The toluene was recovered by live steam distillation.

An effort was made to purify TNT by crystallisation from nitric acid on two continuous-action pieces of equipment. The purification was performed as follows.

124

The TNT was dissolved at 60°C in the mother nitric acid (approximately 70%) taken in 3:1 ratio. The TNT solution was run continuously into a crystalliser with agitator, where the temperature was held at 25 - 30°. The content of the crystallizer then went onto a belt-type cellular vacuum filter. ~~XXXXXXXX~~ Here the product was washed excessively by strong 60%, and ~~EX~~ then by 30% nitric acid, and finally in warm and cold water.

The wash acids were reused, as indicated ~~EX~~(Bibl.75). The strong wash acid was added to the mother liquor, and was also employed to dissolve the TNT. The excess acid was ~~XXXXXXXX~~ diluted with water to separate out the nitro products, which went to the manufacturer of explosive mixtures. The 60% wash acid was added to the 30% that had ~~EX~~ been used for washing. The 30% wash acid was mixed with the wash water.

The TNT thus purified was melted, washed once again with hot water, and then dried.

d) Drying of the TNT

TNT is dried in a separate building, removed to the distance required from considerations of safety, and surrounded with an earth embankment. The drying units consists of a drying bath and a drum for flaking the TNT.

The drying drums consist either of cylindrical vessels (in Germany they were the same as the nitrators) or of rectangular containers. At the bottom of these vessels is a coil for pure steam, and air bubblers. Drying is performed by

blowing compressed air at a pressure of 0.35 - 0.40 atm through a layer of molten TNT heated to 100°C. The spent air escapes into the fan, along with the moisture, through a tube connected to the upper portion of the cover. Beneath the cover there are mounted the sprinkler tubes of a drenching system to drench the TNT in water should it catch fire.

The temperature within the drying apparatus is measured, as a rule, by ~~XXX~~ remote-control thermometer. The volume of the drying bath functioning on this principle should be such as to assure ~~XXX~~ that TNT remains in it for 30 - 40 min. (assuming the layer of TNT to be small).

In Germany, TNT is also dried by blowing through with air, but when this is done the apparatus is kept under vacuum ~~XX~~ (500 mm Hg) and is completely filled with TNT. When the capacity of the apparatus is 15 m³, the drying time is 4 - 6 hrs.

The drying is monitored by means of the freezing ~~XXXXX~~ point of the TNT in a specimen for analysis. If the freezing point proves lower ~~XXXXX~~ than that required (80.2°), which testifies to ~~the~~ inadequate drying, the rate at which the TNT is run in is diminished.

The dried TNT flows from the back into a heated trough beneath the drum for flaking.

The flaking drum is an empty cylinder in horizontal position rotating on two journals, also hollow, mounted in flat end plates. Inserted into the drum is a second, closed cylinder of smaller dimensions, fastened to the center of the external drum in such fashion as to leave between them a free space capable of

being filled with water. The coolant water enters and leaves through the journals.

Beneath the drum is a trough having a steam coil at its bottom. The molten TNT enters the trough from the drying bath by gravity flow, ~~as~~ as stated ~~previously~~ previously. The drum, which is ~~immersed~~ immersed a few centimeters into the molten TNT, rotates, and picks up a film of TNT on its cold surface. The TNT rapidly freezes into a thin crust. The frozen TNT is removed from the drum by a bronze knife and falls into a hopper as flakes. The knife extends across the entire surface of the drum and is pressed close against the generator of the cylinder by means of a weight on an arm of a lever mounted along the axis of the knife.

125 The thickness of the flakes may be regulated in accordance with the intensity of cooling of the drum by the ~~the~~ height of the level of the TNT in the trough beneath the drum, or by the rapidity with which it is rotated.

The drum and the trough are covered with an aluminum hood. Beneath the knife is an aluminum funnel - a hopper carrying a slider that serves to receive the flakes and load them into containers.

It has been proposed that TNT be flaked (Bibl.76) by pouring the molten product through capillary tubes heated to a temperature greater than the melting ~~the~~ point of TNT. The density of such TNT is 0.9 - 1.05 volumetric, and 1.55 - 1.60 absolute.

The flaked TNT is loaded either into wooden boxes or into jute sacks.

Finished first-grade TNT has to satisfy the following specifications. In appearance it must be homogeneous mass of flakes, bright yellow or yellow in color,

without visible impurities or signs of moisture. The freezing point should be not less than 80.2° . The content of moisture and volatiles should be not over 0.07%; the acidity, in terms of H_2SO_4 , should not exceed 0.01%. The content of substances insoluble in benzene or toluene should not be over 0.1%, and oiliness should not be greater ~~than~~ than that of a standard specimen for comparison.

The most important criterion of TNT quality is the freezing point. A high freezing point testifies to the purity of the product and, consequently, to its stability. Another factor, also perfecting the chemical stability both of the TNT itself, and of the shell casing, is the acid content.

The ^{by} termination of the moisture and ~~volatile~~ volatile content in TNT characterizes its explosive properties, as elevated moisture content reduces the sensitivity of TNT to detonation. An increase in the content of insoluble impurities may change the sensitivity of the TNT. Thus, sand as impurity increases the shock and friction sensitivity of TNT. The oiliness of TNT primarily characterizes its sensitivity to a cap detonator.

TNT that fails to satisfy any of these conditions must be rejected. All types of rejects, excluding those due to completely random causes (the introduction of sand by the wind, moistening by water, etc.) represent primarily violations of ~~deviations~~ deviations and ~~deviations~~ from the proper production process.

Reject matter due to high acidity is exceedingly rare. Rejection for freezing point and oiliness may be a consequence both of the inadequate quality of the TNT delivered from the nitration department and of failure to adhere to the proper processes of treatment of the TNT in the crystallizer and the vacuum funnel.

Rejection for oiliness may also be a consequence of inadequate removal of machine oil from the air going to the mixing process in the drying bath.

Rejection because of insoluble residue and color is a consequence of the cleanliness level of ~~XXXXX~~ of the water and the apparatus. When a new apparatus or one that has not operated for some time is started, the color of the first lots of TNT will never be normal. Rejection due to moisture ^{is} a consequence of inadequate drying in the bath (low temperature, poor mixing, excessive speed, etc.).

Rejection due to ~~XXXXXXXX~~ ^{moisture} may be ~~XXXXXXXXXXXXXXXXXXXX~~ recovered by redrying, while rejects for freezing point, oiliness, and insoluble residue may be recovered by recrystallization. Rejects for color cannot be corrected, and this type of TNT is employed to manufacture industrial explosives.

Toward the end of the war, Germany converted to the manufacture of second-grade TNT, with a freezing point not under 79.0°, thus permitting the TNT to be purified by sulfite in the fused condition.

12 The materials required ~~XXXXXXXXXXXXXXXXXXXX~~ in German industry in the production of second-grade TNT were as ~~XXXXXXXXXX~~ follows (per ton of product):

Toluene	0.500 - 0.550 tons
Oilum (recomputed as monohydrate)	2.085 - 2.105 tons
Initial sulfuric acid (recomputed as monohydrate)	0.740 - 0.750 tons
Nitric acid (recomputed as monohydrate)	1.27 - 1.33 tons
Sodium sulfite	0.035 - 0.040 tons
Sodium XXXX bicarbonate	0.010 tons
Electric power	approx. 250 kw hrs
Water	approx. 160 m ³
Steam	approx. 10 tons
Lime (for neutralization of discharged water)	0.200 tons

It must be observed that the irreplaceable losses of sulfuric acid were

210 - 240 kg, and the remainder was reworked ~~in~~ into commercial sulfuric acid.

The consumption of nitric acid was actually ~~up~~ 200 - 250 kg, as that was the quantity that was trapped in the absorption installations.

e) Detoxification of Waste Waters of TNT Manufacture

In connection with the pronounced increase in the production of TNT during World War II, removal of the waste waters acquired major significance. No less important a problem, and intimately interwoven with the former, is that of making use of the TNT byproducts in the waste waters.

In TNT production, waste waters come into being when the TNT is washed to remove acid and to get rid of impurities. In the former case, the water is contaminated with acid and nitro products, although to an insignificant degree. In the latter case, if the sulfite method of purification (the most popular) was employed, the water was contaminated by a considerable amount of nitro ^{product,} ~~substance~~ and was therefore very toxic. On the average, the amount of toxogen in this water came to 80 ~~or~~ 90 kg per ton of TNT manufactured.

It has been found that decontamination of the waste water of TNT production required dilution by not less than 100,000 times. This is possible only when a very large river, or a sea, is available. For this reason, enterprises distant from major bodies of water require special devices for the purification ~~of~~ destruction of the discharged industrial waste water.

First, the discharge waters are sent through a system of traps to pick up the TNT contained in the form of emulsion. There must be separate traps for acid and alkaline waters, as mixing of these waters is impermissible due to the possibility that the highly sensitive explosive substance - dinitrodiazotoluene

sulfenic acid - may be formed.

Methods of purifying discharge ~~waters~~ waters of TNT production that involve electrolysis or reduction of nitro compounds by iron filings are not applicable because of the expense involved. Purification of 1 m^3 of water requires nearly ~~40~~ 40 kw-hrs of energy or 30 kg of iron when the iron-filing reduction method is employed.

In the United States, during the entire period of the war, the discharge waters of TNT plants located near large rivers were emptied into the water. It was found by investigation that, when a given degree of dilution by the river water was attained, this water remained satisfactory for water supply and marine life purposes both in taste, toxicity, acidity, and color.

Where it is not possible to dump discharge waters into large bodies of flowing ~~water~~ water, these waters are evaporated.

In Germany, discharge waters are first ^{neutralized} ~~untreated~~ with soda and then discharged into bodies of water or evaporated and ~~burned~~ burned (Bibi.77). Neutralization is by milk of lime and is carried until the ~~neutral~~-pH of the discharge waters is from 6 - 8. The neutralization installation functions ^{as} ~~is~~ follows.

The ~~wash~~ wash waters from high explosives production go to special settling equipment. The lime for neutralization is slaked in drums, and the milk of lime thus obtained is mixed in tanks and directed, through an automatic regulator, into a labyrinth where it is mixed with the discharge waters. Then, the water goes to a large clarification basin where the gypsum ^{sediment} ~~precipitate~~ that has formed is settled. The sediment is pumped from the basin to a suction filter,

from which it is carried to special pits. The water from the clarification gypsum goes through a coke filter and then flows into a large body of ~~EX~~ water (Bibl.78).

It is then suggested that discharge water be purified by ~~EX~~ ^{wet-process} combustion of the discards in the presence of an iron catalyst at temperatures of 760° or more. By this method, the contaminated water is evaporated in a furnace and the steam is sucked out with air through a metal tube filled with promoter, which is also inside the furnace. The most active promoter is copper chromite (Bibl.79).

A method of biological purification of the industrial waste water by oxidation of the ~~EX~~ impurities by microorganisms has been developed. A serious obstacle to this, however, is the toxicity of TNT production waters for microflora, ~~EX~~ ^{bases} which are the active ~~EX~~ for biological purification. This rapidly results in the death thereof (Bibl.79).

Recently, the purification of industrial waste water has come to be performed by ~~EX~~ ion-exchange resins (Bibl.80). This is apparently applicable to discharge waters of TNT production.

f) Safety and Labor Protection in TNT Production

In addition to the safety rules common to all types of manufacturing, three special problems: the danger of explosion, fire danger, and poisoning, have to be considered in TNT production.

The danger of fire in TNT production arises from a number of factors:

a) The possibility of ignition of the TNT, particularly in the drying process and in long-term contacts with the heated body (the walls of the steam coil, steam pipes, etc.) which causes decomposition thereof;

b) The possibility of ignition of toluene and mononitrotoluene by a spark, inasmuch as the detonation temperature of toluene is 7.7° , and the flash point is 54° ;

c) The danger of ignition of the toluene upon contact with the melange or with nitric acid fumes.

The following physiological consequences of TNT manufacture exist:

a) Effects of nitrogen oxide and nitric acid ~~XXXXX~~ fumes upon the blood and protoplasm (maximum permissible concentration 0.005 mg/ltr computed as N_2O_5);

b) The effects of toluene fumes upon the blood, upon the respiratory organs, and upon nerve cells (maximum permissible concentration 0.1 mg/ltr);

c) Sulfuric acid fumes (SO_3 from oleum) upon mucous membrane (maximum 0.02 mg/ltr);

d) TNT dust (maximum permissible ~~XX~~ 2 mg/m³).

Moreover, sulfuric acid, nitric acid, ~~and~~ spent acid, and acid water produce skin burns.

In accordance with the ~~XXXXXXXXXX~~ forgoing, the rooms and buildings in which TNT is manufactured have to be fireproofed to a maximum, convenient for servicing the process, and ~~XX~~ of the least possible height. All ~~XXXXXXXX~~ shops (nitration, purification, drying, storage) have to be surrounded by earthen embankments. The ~~XXXX~~ buildings should have a ~~XXXXXX~~ lightweight front, large windows and a roof that can readily be knocked off. The doors and staircases must be such as to permit rapid evacuation of personnel if necessary, so that each work position has access to not less than two exits, and the distance to the exits is not ~~XX~~ more than 15 m. Artificial light must be provided by sources providing no danger of explosion.

Ventilation should be such as to assure the absence ~~of~~ ^{of} dangerous gases, fumes, and dust from the air, or a content thereof not greater than the permissible maximum. In nitrators, drying baths, and other similar apparatus, ~~the~~ individual gas suction must be provided.

To prevent possible fires, toluene containers must be outside of the ~~buildings.~~ ^{first-stage} buildings. The ~~XXXXXXXXXX~~ and second-stage nitrators and separators should have devices for delivery of carbon dioxide in case of fire. The dryer room should have a drencher system of fire control. Hydrants should be provided inside all buildings, and the water system both in the buildings and in the yards must permit pumping in either direction.

Gases from the apparatus which are to be absorbed are collected in two separate collectors: the first for gases from the first-stage apparatus, and the second for second- and third-stage apparatus, to prevent contact between the toluene fumes and those of strong nitric acid. The condensate from these collectors is assembled in different containers.

The basic measure to prevent explosions is strict adherence to the technical flow sheet.

Nitration, as ~~XXX~~ has already been noted above, is an exothermic reaction, which is, moreover, accompanied by oxidation and hydration of the sulfuric and nitric acids by water formed in nitration and oxidation, as a consequence of which the overall heat effect virtually doubles. To maintain heat equilibrium in the system, the nitrators are provided with powerful cooling devices - jackets and coils. Violation of heat equilibrium may be caused by cessation of delivery

of the coolant or by improper conduct of the process.

When ~~the~~ the reaction is slowed (as a consequence of reduced temperature or inadequate concentration of one of the components), components not entering into the reaction will accumulate in the apparatus, and this may result in a rapid increase in temperature, which will ~~then~~ already not be capable of being controlled by cooling. In the first and second stages of nitration, the situation may result in expulsion of nitro mass and fire, and in the third stage may even result in explosion. Therefore, the unreacted components in the nitration bath must be held to concentrations that are less than dangerous.

In the first and second stage of nitration, the nitration velocity is great, at the accepted temperature regime and activity of the acid mixtures. Reaction between the components ~~is~~ ends almost entirely when they are drained out. In the third stage, nitration velocity is considerably slower, and therefore, when the components are metered in, it is necessary ~~to~~ to make sure that ~~concentrations~~ concentrations do not reach a ~~dangerous~~ dangerous state. In determining what concentration is safe, it is necessary to take as one's ³ point of departure that, if cooling ceases, the temperature of the nitro mass, when one of the components has ~~reacted~~ reacted in its entirety (usually, this is the nitric acid), shall not rise above ^a that level (120°) beyond which intensive ~~oxidation~~ processes of oxidation set in.

In the third stage of nitration, entry of oil, rags, and other objects of ~~highly-oxidizable~~ highly-oxidizable material into the nitrator is very dangerous, as the highly-concentrated acid mixture may cause them to become carbonized and to ignite.

In running the process, the apparatus man must ~~keep~~ give prime attention to the temperature and must control it. ~~When~~ ^{If} the temperature should jump to its maximum, the run-in of components must be cut down or stopped, and 129 if the temperature in the apparatus in the third stage should jump to over 150°, the contents of the apparatus must be dumped into an emergency tank filled with water, and compressed air must simultaneously be directed therein.

Stirring in nitrators must be assured by two energy sources operating independently and switching automatically from one to the other, and if the agitator should stop suddenly, delivery of the components must stop, and more intensive ~~emergency~~ cooling must be cut in.

To reduce the possibility of ~~spontaneous~~ spontaneous combustion of the TNT and the intermediates of production thereof, care must be taken to provide systematic removal of explosive residues from the apparatus. It is also necessary that the apparatus have no spots where substance can accumulate in stagnant form during the process, or spots difficult of access for cleaning. These "dead zones" are the most probable areas of spontaneous combustion.

In all apparatus in which explosives are present at high temperature (nitrators, lime baths), instruments must be installed for automatic regulation of the temperature, and to signal an increase therein above a specific level.

The presence of certain impurities may also increase tendencies ~~to~~ to spontaneous combustion. This tendency is furthered most strongly by those impurities contained in TNT waste, as the majority of instances of spontaneous combustion in TNT production has had to do with the retreatment of wastes. These

~~These~~ products not only ignite readily, but their combustion proceeds to detonation particularly readily. It is also necessary to bear in mind the elevated sensitivity of heated explosives to mechanical effects. This is often the prime cause of accidents in manufacture.

Once the explosive has begun to burn, this combustion may proceed quietly to completion, but it may also terminate in detonation. A combustion of high explosives is less intensive at the outset, and it is therefore possible to control the ~~fire~~ ^{fire} at the moment that it arises.

Fires in nitrators and separators are controlled by stirring the batch with an agitator or, in extreme cases by air. TNT that has caught fire in the drying bath is doused with water. Nitrators and separators have ~~the~~ to have a dependable apparatus for dumping the batch into specially-provided reservoirs, filled with water.

The charging of the components must be in block with stirring so that a cessation of agitator motion automatically stops charging. Each nitrator must be equipped with a device that clearly shows whether the agitator is working, and if delivery of electric power ceases, the agitator motor must automatically switch to other power source.

Every four weeks, the cooling coils must be tested to determine whether they are still leakproof, by a test pressure of not less than 5 atm.

The lines serving to deliver the nitro ~~compounds~~ compounds in liquid form should not bend (or sag). They must be laid ~~with~~ with sufficiently ~~uniform~~ uniform slope so as to make it impossible for the nitro compound therein to stagnate. Valves and cocks on the pipelines must be so designed as to make it impossible for

explosive residues to collect in "dead zones".

To localise explosions within a shop, it is desirable to surround not only the drying shop, but the purification and nitration shop with an earthen embankment. The output capacity of shops in which there is a danger of explosion should be limited.

A number of measures were taken at the German TNT plants to install automatic locking and automatic monitoring of the technological process. The nitration shops had automatic (or hydraulic) component delivery breakers, to act if the agitators ceased operating. Contact resistance thermometers in block with emergency signaling systems were installed in the nitrators. These thermometers function at two limiting temperatures in the third-stage nitration nitrators: a lower limit of 76° and an upper of 96°.

All the ~~nitration~~ nitration shops had emergency tanks with water for cooling, should the delivery of water cease from pipelines, which in turn ~~were~~ ^{were} cut off automatically when the pressure in the water system dropped. In all shops presenting any danger of fire, a sprinkler system was provided. In addition, inert gas was delivered to certain types of apparatus (such as the TNT drying apparatus).

The production shops were usually built of small size. The plants had several identical parallel shops. The nitration shops for production of mononitrotoluene, dinitrotoluene, and TNT were separate (not under a single roof). In buildings where large amounts of explosives were concentrated, the basic equipment was sunk below ground level.

B. Dinitrobenzene and Other Benzene Nitro Derivatives

Of the nitro derivatives of benzene, only dinitrobenzene has even a limited use as an explosive. It is a weak explosive, and is, moreover, quite toxic. Trinitrobenzene, an explosive more powerful than TNT, is not produced on an industrial scale because of the difficulty of introducing the third nitro group into the dinitrobenzene. This renders the employment of benzene for the production of explosives irrational, despite the fact that its availability in natural sources (petroleum and coal) is almost seven times as great as the content of toluene, which is widely employed for the manufacture of TNT.

The following data permits one to judge the scale of utilization of benzene for production of explosives. During the First World War, the production of dinitrobenzene in Germany was 27% of the total quantity of nitro compound; but during the Second World War it was only 5.5%.

In 1944, the following were produced from benzene (in tons):

Dinitrobenzene	15,000
Picric acid	3 000
Hexyl	7 000

IX Sixteen thousand tons of benzene were expended in the production of these explosives. However, the bulk of this was employed to produce synthetic toluene, on which 43,200 tons of benzene was expended per year. Synthetic toluene obtained from benzene and methanol is very expensive, and this was sharply reflected in the cost of the TNT.