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Studies on Nitration of Starch Stabilization and Explosive Properties of Starch Nitrates

THESIS

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This work is dedicated to my
Professor Dr. Heinrich HOPFF
to whom I am greatly indebted
for his invaluable help and encouragement

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INTRODUCTION

In recent years, nitration in the presence of acetic anhydride was industrially established. A group working under Bachmann at the University of Michigan developed a new method for the production of RDX which is designated as the combination process. It constitutes the nitration of hexamethylenetetramine with a mixture of nitric acid and acetic anhydride in the presence of ammonium nitrate. Wright, of the University of Toronto prepared DINA by the nitration of diethanolamine in acetic anhydride containing a small amount of chloride.

However, an investigative study of the nitration parameters has not yet been published. Thus it seemed promising to undertake a study on the nitration of starch with nitric acid in the presence of acetic anhydride to evaluate the effects of temperature, time, and medium compositions on the degree of nitration of the product.

Part I deals with the basic raw material starch, its composition and properties, and the fractionation into its chief constituents, namely, amylose and amylopectin. The nitration studies have been conducted on these latter relatively pure components.

In part II, two fundamental aspects of starch nitration are discussed in detail. The evaluation of the nitrating capacity of nitric acid-acetic anhydride mixtures is of primary importance, since such an investigation has not been published before. A study of the nitration parameters of nitric acid-pyridine mixtures has also been studied, for such mediums are known to possess relatively weak nitrating power in contrast with the former mixtures which possess relatively high nitrating activity.

The newly studied method of nitration of starch with nitric acid in the presence of acetic anhydride necessitated a study of the conventional purification treatment which includes boiling the starch with water for various lengths of time. Part III deals with the stabilization of nitrated starch by boiling in both slightly acidic and slightly alkaline mediums, as well as by fractionation of starch nitrates with alcohol.

Part IV describes the exsisting methods of testing explosives for sensitivity and performance. It includes a new study of the sensitivity of starch nitrates to initiation as well as impact and frictional-impact. In evaluating the performance characteristics of starch nitrates, the determination of power, brisance, and speed of detonation have also been carried out.

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Part I

STARCH

A. THEORETICAL

1. Composition and properties of starch (1)

Starch is formed as a result of assimilation in the chlorophyll containing parts of plants. The starch grain consists mainly of a mixture of carbohydrates readily hydrolizable to glucose. This mixture of carbohydrates which constitutes the commercial grades of starch is by no means homogeneous.

1.1 Constituents of the starch grain

The starch grain contains 10-20% water, 0.01-0.05% nitrogen, 0.003-0.038% phosphorus, 0.04-0.83% fat, silica and metal compounds. Water is bound to the lattice, since strongly dried starch grains are amorphous and do not show the typical interference rings in the X-ray diagram. Nitrogen is present as a protein which is not chemically united with the carbohydrate portion, but union exists by coacervation. The protein may be combined with phosphoric acid which is estrified to the carbohydrate portion to form a phospholipid. Phosphorus is present as phosphoric acid esterified with the carbohydrate portion, and the phosphate is unevenly distributed in the different components constituting the carbohydrate portion of the starch grain. The fatty material is either adsorbed by the starch grain, in which case it can be ether extracted, or, esterified with the carbohydrate portion. On hydrolysis, palmetic, oleic, linolic and linolenic acids are obtained. Silica is present in traces which collect with the less soluble fraction of the starch grain. Silicic acid may be present, esterified with the carbohydrate portion.

The carbohydrate portion, which is the chief constituent of the starch grain, is partially soluble in boiling water. The insoluble part, however, absorbs a certain quantity of water, thus forming an elastic gel without passing into solution. The soluble fraction is referred to as amylose and the insoluble one as amylopectin. Apart from the difference in solubility, dissolved amylose and swollen amylopectin have many features in common. They are hydrolyzed by the same enzymes to give mostly glucose and exhibit practically the same optical rotation.

1.2 Fractionation of the carbohydrate portion of the starch grain

Several methods have been attempted to fractionate starch into its amylose and amylopectin components. They include precipitation of amylopectin by salts of alkaline earths, treatment with superheated steam, treatment with water at 70° to 90°C, centrifugation, freezing, electrodecantation, ultrafiltration, selective adsorption, and alcohol precipitation.

1.2.1 Fractionation by hot water

Hot water brings about loosening of the grain structure, thus permitting loosely bound molecules to be extracted. Straight chain amylose molecules have the ability to diffuse outside the swollen grain, while branching in amylopetin molecules nullifies its rate of diffusion.

By extracting a 2 per cent starch paste at 70°C, Meyer found that 33.1% of the total starch could be leached out after 370 hours. At 80°C, 16% could be leached out after 1 hour, 33.2% after four hours, and a maximum of 35.4% after nine hours.

1.2.2 Fractionation by adsorption

The selective adsorption methods employ activated carbon, Fuller's earth, or cotton cellulose for preferential adsorption of amylose. When a starch paste is brought into contact with cotton cellulose, a cotton cellulose adsorbate is formed. This adsorbate is readily decomposed by boiling water to give a clear solution of amylose which can be concentrated under vacuum and the amylose precipitated by ethanol.

1.2.3 Fractionation by precipitation with alcohols

It was found that butanol, pentanol, and butanol-methanol mixture, have a selective precipitating action towards starch sols. Thus the amylose constituent of starch is precipitated leaving the amylopectin in solution. However, both the precipitated amylose and the non-precipitated amylopectin are contaminated with small amounts of the other.

1.3. Chemical structure and properties of amylose and amylopectin

With reasonable degree of certainty, the evidence at present leads to the conclusion, that the starch molecule is built up of D(+)-glucose units. Meyer, Hopff, and Mark showed that these units exist in the alpha form of the pyranose ring structure and are bonded together through oxygen bridge atoms in the 1,4-positions to form the thread-like molecules which constitute the starch. Meyer designated the straight chain structure of starch as amylose and the branched chain structure as amylopectin. Amylopectin is characterized by a periodic branching at the 3,6-positions of a side chain of about twenty 1,4-alpha-D(+)-glucosyl units.

The molecular weight of amylose corresponds to about 200-1000 glucose residues with only one non-reducing end group. On the other hand amylopectin contains about 1500 or more glucose residues with one non-reducing end group for every twenty to thirty glucose residues. It is apparent that there are from two to four hydroxyl groups per glucose unit, of which three are predominating, and capable of undergoing esterification reactions. Thus, nitration of starch, for example, gives a series of reaction products namely:

Starch mononitrate	$C_6H_9O_4ONO_2$	corresponding to	6.76 % nitrogen,
Starch dinitrate	$C_6H_8O_3(ONO_2)_2$	corresponding to	11.11 % nitrogen, and
Starch trinitrate	$C_6H_7O_2(ONO_2)_3$	corresponding to	14.14 % nitrogen.

The distinguishing differences between amylose and amylopectin lie in the facts that amylose is practically completely digestible (100 %) with beta-amylase while amylopectin is only 50 % digestible. With iodine, amylose gives a pure deep blue coloration and amylopectin a purple to reddish coloration. When starch is titrated with iodine potentiometrically, only amylose fractions absorb large amounts of iodine and the amylopectin fractions do not take up iodine. Amylose is completely crystallizable with butanol or other crystallizing agents, while

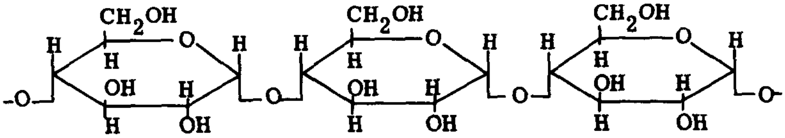


Figure 1 a Straight chain amylose structure

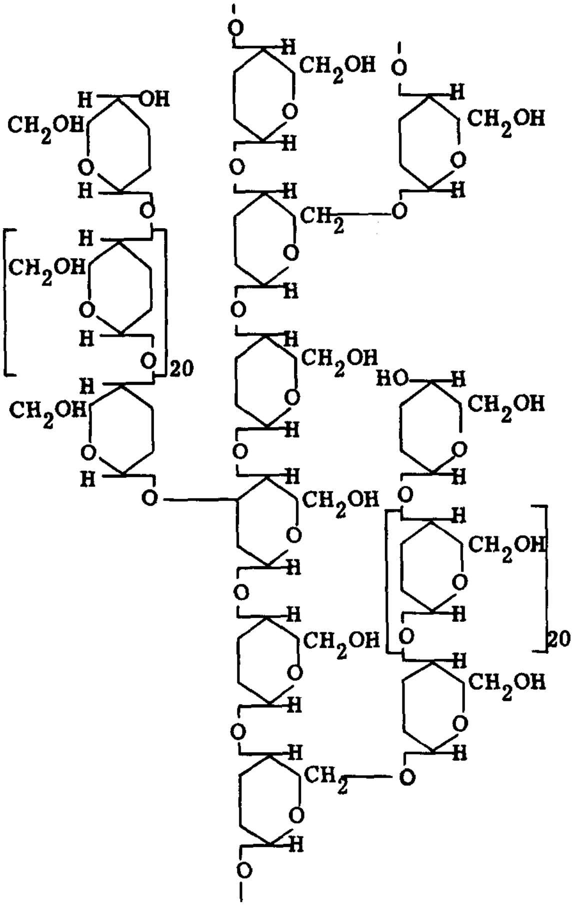


Figure 1 b Branched chain amylopectin structure amylopectin which does not form a crystalline complex, gives patterns of poor crystallinity. Furthermore, amylose exhibits low solution stability and at low temperature undergoes the phenomenon of retrogradation while amylopectin exhibits quite the reverse.

1.4 Physical structure of the starch grain

Meyer showed in his classical work on the starch grains that they are composed of tangentially disposed layers which consist of radially arranged, crystalline, elongated particles giving a trichite structure. The layers contain crystalline micells arranged perpendicularly to the plane of the layer. The crystalline regions consist of starch chains or portions of such, and the crystallites are united by amorphous chains. This system of crystallites united by molecular threads is built up from the giant branched molecules of amylopectin.

Kast and his co-workers have shown that starches offer a variety of types of diffraction patterns. The two extremes of crystal structure exist which are designated as "A" and "B" configurations. Types between the "A" and "B" extremes are designated as "C" configuration. It is evident that there is ring-for-ring correspondence between the "A" and "B" extremes which indicates that the diffractions are those of a single major component of the starch grain.

Starch pastes crystallize to give "A", "B" or "C" types of crystal structure depending on the temperature of the preparation. Generally, the "B" type of crystallization is obtained at room temperature, the "C" type at temperatures above room temperature, and the "A" type at 80^{0} to 90^{0}C. At higher temperatures amorphous preparations are obtained.

Precipitation crystallization of starch pastes with ethanol and propanol gives a "V" configuration "Verkleisterungsspektrum", which is simpler than the "A" and "B" configurations. The X-ray diagram of butanol precipitated amylose has shown that the amylose chains form helical coils, persumably around the alcohol molecules, and the cylinderical molecules then pack closely with the formation of characteristic rectangular platelets and hexagonal rosettes of the butanol precipitate. In amylopectin, the frequent branching interrupts the regularity of the amylose chain and prevents the molecule from precipitating in the helical cylinderical crystallization.

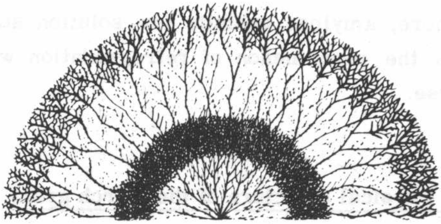


Figure 2 **Meyer's** trichite structure of the starch grain

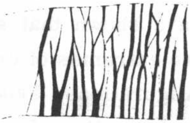


Figure 3 Arrangement of crystalline micelles (thick lines) and the primary valance chains uniting these in a single layer of a starch grain

Figure 4 Open net work structure of swollen amylopectin. The crystalline regions acting as points of linkage are indicated by thicker lines

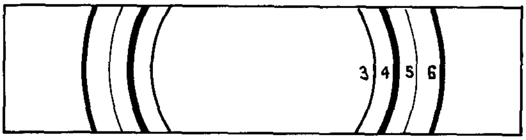


Figure 5 "A" pattern of cereal starches

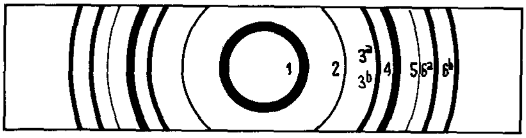


Figure 6 "B" pattern of tuber starches

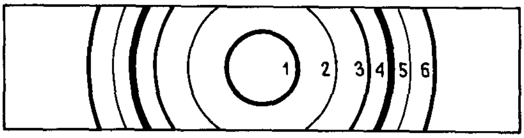


Figure 7 "C" pattern of fruit starches

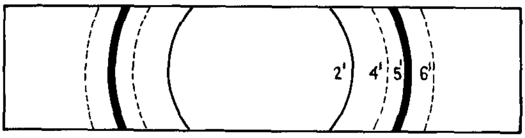


Figure 8 "V" pattern "Verkleisterungs-spektrum" of alcohol precipitated starches

B. EXPERIMENTAL

2. Examination and treatment of starch

2.1 Raw material

The material employed in this work is Egyptian rice starch which is manufactured by The National Starch Company of Alexandria, Egypt. The following sketch outlines the process of its manufacture.

RICE
↓
Steeping in 0.7% sodium hydroxide solution
↓
Washing with water
↓
Grinding with 0.2% sodium hydroxide solution
↓
Centrifugation
(to separate small fibres an impurities)
↓
Ultracentrifugation
(to separate the glutin)
↓
Starch milk
↓
Neutralization with suphuric acid
↓
Centrifugation
↓
Drying
↓
Grinding

2.2 Chemical analysis of the starch

The chemical analysis of the minor constituents of the starch is as follows:

Water	12.65%
Nitrogen (Kjeldahl)	00.18%
Phosphorus	00.00%
Ash	00.22%
Fatty material (Ether extract)	00.29%

2.3 Fractionation of the starch

Meyer and his co-workers (2) introduced the hot water fractionation technique of the starch grain. They found that the swelling is practically zero in fifty parts of water at 60°C. However, at 70°C a marked swelling is brought about and the diameter of the grains becomes 2.5 times larger; at 80°C the diameter of the grains is tripled; and at 90°C the grains burst. The quantity of substance passing into solution after one hour of extraction is 16.5% at 80°C and 7.7% at 70°C.

The mechanism involved in fractionation by hot water is the loosening of the grain structure and the extraction of molecules not too tightly bound or entangled in the network. The amylose molecules are able to diffuse slowly out of the swollen grains, while branching in the amylopectin molecules tends to reduce its rate of diffusion to practically zero. It is reasonable to suppose that the fractionation will not be complete, since some of the straight chain amylose molecules will be so hopelessly entangled that their rate of diffusion out of the structure will be very slow. On the other hand, many of the amylopectin molecules on the surface of the grain will be torn loose and will appear as an impurity in the amylose.

2.3.1 Extraction at 80°C

Meyer and his coworkers presented the following procedure for extracting starch at 80°C. A mixture of 20 grams of dried maise starch in one liter of water at 80°C is slowly agitated for one hour (rapid agitation causes the grains to burst). The liquid is then removed by centrifugation and the swollen grains treated again for one hour in the manner described above. The treatment is repeated for eleven times and the results are given in table 1.

Table 1

Period of extraction (hours)	Weight of extracted starch per operation (grams)	Total extracted starch per cent
1	3.2	16.0
2	1.16	21.8
3	1.59	29.8
4	0.7	33.2
5	0.28	34.6
6	0.08	35.0
7	0.02	35.1
8	0.02	35.2
9	0.03	35.4
10	0.00	35.4

2.3.2 Preparation of amylose

In a glass beakter, 1500 cc. of deionized water are heated to 80°C in a thermostatically controlled water bath equiped with a stirrer revolving at 10 to 15 rpm. Thirty grames of rice starch dried at 105°C for 3 hours, are added in small quantities over a period of five minutes. After an extraction period of one hour the liquid is poured into a long glass cylinder, and allowed to settle. After five hours, 1100 cc. of the faintly turbid upper layer are removed by syphoning and the swollen material remaining in the bottom of the cylinder is repeatedly extracted in the same manner. The syphoned faintly turbid upper layers are concentrated after each extraction to about 100 to 200 cc. under vacuum (20 to 25 mm.) at a bath temperature not exceeding 55°C. The material from these extracts is quantitatively precipitated by the addition of an equal volume of ethanol, and separated as a fine white precipitate by centrifugation. The material is then washed with 80% ethanol, centrifuged, and dried. The yields of the dry material are given in table 2.

Table 2

Extraction	Weight of alcohol precipitated extract in grams (Mean of ten extractions)	Yield %
First	4.71	15.7
Second	1.89	6.3
Third	1.81	6.0
		28.0 total

The material extracted in this manner is conventionally referred to as amylose in this work.

2.3.3 Preparation of amylopectin

The swollen material remaining after the third extraction is repeatedly extracted in the same manner for three more times. Then the liquid is removed by centrifugation and the remaining material treated successively with alcohol and ether and finally dried. This material is conventionally referred to as amylopectin in this wordk. Yield is 19.12 grams or 63.7%.

Part II

NITRATION OF STARCH

A. THEORETICAL

1. Historical review

The question related to the preparation of a nitric acid ester of starch, the so called nitrostarch, or more precisely starch nitrate, is one of the most comprehensively studied problems (3).

1833. The earliest attempt to prepare nitrostarch appears to have been in 1833, when Braconnot (4) treated starch with concentrated nitric acid. He found that starch dissolves in the acid. On dilution with water, the liquid gives a curdy precipitate of material which, after washing, dries out to a white pulverulent mass. This material, to which Braconnot gave the name "Xyloidine", takes fire very readily.

In the same year, Liebig (5) argued that one cannot state wheter the treatment of starch with concentrated nitric acid gives a simple organic substance or not. He concluded that the material should be analyzed for certainty.

1838. Pelouze (6) studied xyloidine further. He found that if starch is dissolved in concentrated nitric acid of specific gravity 1.5, and if the solution is diluted immediately with water, xyloidine is precipitated and that the acid filtrate on evaporation yields practically no residue. If the mixture is allowed to stand for two days, the xyloidine is completely destroyed. Pelouze considered xyloidine to be a nitrate of the starch formed from the reaction between one equivalent of starch and one equivalent of nitric acid, accompanied by the elimination of one equivalent of water. He observed that it is readily cumbustible; that it ignites at 180^{0}; and that it burns with considerable violence, leaving practically no residue. He misjudged the product of the action of nitric acid on paper to be xyloidine till Schönbein announced the discovery of guncotton.

1844. Buijs-Ballot (7) described in detail the preparation of xyloidine, and gave some consideration to its constitution. His results of analysis corresponds to the emperical formula $C_{12}H_{18}O_9 + N_2O_5$.

1845. Gerhardt (8), when discussing the results of Ballot's analysis did not adopt his formula. He supposed that the nitration of starch yields a mixture of a mononitrate $C_{12}H_{18}O_{10}NO_2$ and a dinitrate $C_{12}H_{18}O_{10}(NO_2)_2$.

1846. Pelouze (9), after Schönbein's discovery of guncotton, critically examined both xyloidine an guncotton, which he called "Pyroxyline". He found that they differ with respect to both their chemical composition and physical properties.

1847. Gladstone (10), by exercising special precautions, was able to carry out combustion analysis of xyloidine and pyroxyline. The pyroxyline is found to contain 12.75% nitrogen and is thought to correspond to a pentanitrate, while xyloidine corresponds more nearly to a trinitrate.

In the same year, Kindt (11) reported a microscopic study of the transformations which accompany the reaction of mixed acid on starch, and Payen (12) verified the preparation of xyloidine by earlier workers. By conducting reactions under the microscope, the latter worker observed that the starch granule consists of an inner and an outer portion.

1853. Béchamp (13) found that starch could be regenerated from xyloidine by treating the latter with ferrous salts.

1856. Béchamp (14) studied the action of concentrated nitric acid on starch under different conditions to obtain intermediate reaction products. He found that when starch is treated with three parts of nitric acid for twenty four hours at about 20^{o}, the mass remains viscous. After some hours, as oxidation proceeds, the mass becomes transparent and on addition of alcohol the regenerated soluble starch is precipitated.

1861. von Uchatius (15) described the preparation of starch nitrate by dissolving starch in eight parts of concentrated nitric acid and allowing the mixture to stand at room temperature for one hour. The resulting viscous mass is poured with vigorous stirring into sixteen parts of concentrated sulphuric acid; and after twelve hours, the starch nitrate is precipitated with water, washed, and dried.

1862. Béchamp (16) showed Braconnot's xyloidine to be a mononitrate and gave it the formula $C_{12}H_9O_9, NO_5$. This mononitrate is partially soluble in an alcohol-ether mixture, giving a soluble mononitrate and an insoluble mononitrate differing in their molecular states. He prepared also a dinitrate of starch and gave it the formula $C_{12}H_8O_8, 2NO_5$. This dinitrate is again fractionated by alcohol to give a soluble and an insoluble component. He decomposed all of these nitrates by the action of ferrous chloride to regenerate the starch with the liberation of nitric oxide. The rotary power and deflagration temperature of all are determined.

1875. Reichardt (17) examined soluble starch prepared by the action of nitric acid on starch. He found that one part soluble starch dissolves in forty parts of water at 20°C. He studied the action of fuming nitric acid on soluble starch and found that it gives a mononitrate of the emperical formula $C_6H_9(NO_2)O_5$, which is different from nitrostarch in the respect that it is soluble in alcohol and ether.

1891. Dynamit Nobel AG (18) patented a process for the manufacture of nitrostarch. Dried starch is dissolved in ten parts of nitric acid of specific gravity 1.501 at 20 to 25°C with continuous stirring. The dissolved starch is precipitated by a mixed acid containing 70 per cent sulphuric acid monohydrate and 10 per cent nitric acid monohydrate as may result from the manufacture of nitroglycerin. The precipitated nitrostarch is filtered, washed, and treated with soda solution.

1892. Mühlhauser (19) reviewed the history of the prepartion and properties of the nitric acid esters of starch. He considered the nitrostarch of Braconnot to be a dinitrate and that of Béchamp a tetranitrate. He gave the following compositions to the different stages of the starch nitration products, namely,

$C_{12}H_{16}O_6(ONO_2)_4$	for starch tetranitrate	containing 11.11% nitrogen.
$C_{12}H_{15}O_5(ONO_2)_5$	for starch pentanitrate	containing 12.75% nitrogen.
$C_{12}H_{14}O_4(ONO_2)_6$	for starch hexanitrate	containing 14.14% nitrogen.

He showed that the product of the action of nitric acid on starch is not a nitro compound but a true ester, and he prepared a tetranitrate containing 10.58 to 10.50 per cent nitrogen by the action of nitric acid of specific gravity 1.501 on dry rice starch. By the action of mixed acid, he was able to prepare a nitrate which is partially soluble in an alcohol ether mixture. The insoluble portion is found to be a pentanitrate containing 12.76 to 12.98 per cent nitrogen, while the soluble portion contains only 10.45 per cent nitrogen. The hexanitrate is prepared by the action of concentrated nitric acid on dry starch and the product is precipitated after twenty four hours by the addition of concentrated sulphuric acid. The product contains 13.52 to 13.22 per cent nitrogen.

1898. Will and Lenze (20) nitrated starch by two different methods. Starch is added with cooling to ten volumes of fume expelled nitric acid of specific gravity 1.52. After twenty four hours nitrostarch is precipitated by the gradual addition of concentrated sulphuric acid to yield a product which after washing with water followed by alcohol, contains 14.04 per cent nitrogen. By a second method, starch is added to mixed acid and kept at 8°C for twenty four hours. The nitrostarch is precipitated by the addition of ice cold water to yield a product which, after stabilization, contains 13.90 per cent nitrogen. These derivatives are soluble in both alcohol and ethyl acetate.

In the same year, Syniewski (21) prepared a nitric acid ester of soluble starch by the action of fuming nitric acid, the product being soluble in acetone. He also studied the effects of oxidizing agents on soluble starch nitrate.

1899. Brown and Millar (22) prepared nitrates of starch containing from 7.8 to 11.5 per cent nitrogen. Determination of molecular weight by the lowering of the freezing point of acetic acid gives values of approximately 987. When these derivatives are treated with ammonium sulphide, soluble starch is regenerated.

In the same year, Moffatt (23) patented a process for producing a nitrate of starch consisting of mixing dry starch with mixed acid below 4°C. After nitration the product is precipitated with ice water till the specific gravity of the diluted acids is 1.30. After washing, the product is boiled with an alkaline lye sufficient to maintain a distinct alkaline reaction until soluble matters are dissolved, the material then being washed and dried.

1903. Saposchnikov (24) reported the preparation of nitrates of starch containing 13.4 per cent nitrogen by two different methods. Molecular weight determination by the ebulliometric method gives a value of 1845.

1904/5. Hough (25) claimed the preparation of an octanitrate of starch corresponding to the formula $C_{12}H_{12}(NO_2)_8O_{10}$ which is theoretically faulty. He used oleum in preparing the mixed acid so as to maintain about 2 per cent free sulphur trioxide in it. His product is insoluble in alcohol, ether, and easily soluble in an ether-alcohol mixture. It contains about 16.5 per cent nitrogen.

1906. Arnold, Fox, Scott and Roberts (26) patented a method for manufacturing nitrostarch consisting of adding a preparation of starch and nitric acid to sulphuric acid or waste acid from the nitrocellulose manufacture so as to obtain the precipitate of nitrostarch in the form of a flaky mass which is freed from acid and washed in a vessel containing a discharge opening at the bottom.

1908. Berl and Smith (27) decomposed the nitric acid ester of the starch by treatment with alcoholic sodium hydroxide. On acidification of the reaction mixture, they obtained a product whose osazone resembled that obtained from oxypyruvic acid.

1910. **Berl** and **Butler** (28) investigated the method of **Hough** previously described for the preparation of nitrostarch. **Hough** had claimed the preparation of a product containing 16.38% of nitrogen, using oleum to maintain about 2% free sulphur trioxide in the acid mixture during nitration. This would correspond to 16 nitric radicals in the molecule $C_{24}H_{40}O_{20}$ whereas other investigators have shown not more than 12 radicals corresponding to 14.14% nitrogen. **Hough's** method is followed exactly using starch from various sources. His results as to nitrogen content are not confirmed, but intersting values are found for the solubility in alcohol ether mixtures, hygroscopicity, ignition point, and viscosity of the products. These results are summarized in table 3.

Table 3

Variety	N %	Ig. pt.	Solubility	Relative viscosity 1% (acetone = 1)
Wheat starch	13.23	121	Slightly sol.	2.00
Potato starch	13.44	120	Slightly sol.	1.37
Rice starch	12.86	135	Soluble	1.26
Soluble starch	13.35	120	Soluble	1.16

A comparison is made with cellulose under the same conditions of nitration and it is found that cellulose nitrate contained 13.40% nitrogen with a relative viscosity of 95.1, whereas potato starch nitrate contained 13.44% nitrogen with a very low relative viscosity amounting to only 1.75. This remarkable difference in viscosities can be explained by the difference in the molecular size and weight between cellulose and starch. The starch nitrates are pure white, soluble in concentrated sulphuric acid an more hygroscopic than cellulose nitrates of equal nitrogen content. Combined sulphuric acid of about 0.5% is found in the starch nitrates.

1911. **Dymond** (29) patented a process for the nitration of starchy material. It consists in mixing rosin and finely ground or pulverized wheat, together with boiling water. The cooked mass is treated with strong nitric acid and then freed from nitric acid by boiling water.

In the same year, **Ellis** (30) patented an apparatus for nitrating starch consisting of a nitrating tank, receptacles for the nitrating acids and the material to be nitrated with connections therefrom to the nitrating tank encircled with cooling coils. The finely divided starch is forced through the supply connection into the closed nitrating tank with the aid of a blower. In the nitrating tank, a hood directs the particles downward into the acid.

<u>1917</u>. Sadtler (31) patented a process for the production of stable nitrostarch which consists of treating the starch for two to four hours with cold 1.5% solution of sodium hydroxide equal to two per cent of the weight of starch to remove oil and proteins as well as swell the starch granules. Then the starch is rinsed with several changes of water, agitated with a two per cent solution of bleaching powder, washed with water, slightly acidified with hydrochloric acid, and dried. The purified starch is then nitrated with a bath containing 65% sulphuric acid, 25% nitric acid, and 10% water. The nitrated product is boiled with aqueons sodium carbonate solution and finally subjected to prolonged washing with water.

<u>1920/1</u>. Anchors (32) patented a process consisting in baking cereals such as wheat, corn or rice until they puff or swell; and these are then treated with a mixture of 64% sulphuric acid, 30% nitric acid, and 6% water at a temperature of about $5^{o}C$ to effect nitration of the starch contained in the material. The acid mixture is supplied to the bottom of a receptacle containing the cereal which tends to force out the air occluded in the material and prevents local heating. The porous condition of the material due to puffing facilitates rapid and uniform nitration. The buffed material is sufficiently buovant that it floates on the spent acid and washing water. The washed nitroproduct is repeatedly boiled for twelve hours in a 0.5% solution of sulphuric acid and is stabilized by the addition of a small amount of sodium soap or other fatty acid salt, followed by a repeated washing with water and centrifugation.

<u>1926</u>. Bronstein (33) patented a process for drying nitrostarch which consists of filling a relatively long tubular fabric bag, with a slurry of nitrostarch and exposing the bag to a drying atmosphere until the evaporation of the moisture from the surface of the bag has reduced by capillarity the moisture content of the contained nitrostarch to the desired extent.

<u>1927</u>. Okada (34) investigated the method of nitration of starch, the denitration, the swelling, and the sulphuric acid ester contained in nitrostarch. By either the direct nitration of starch with mixed acid or the indirect method newly proposed by Okada, which consists of preliminary treatment of starch with a certain medium before subjecting it to the ordinary nitration, nitrostarch containing 13% of nitrogen can be obtained. During both nitrations, the starch undergoes

no more damage caused by the action of hydrolysis or oxidation of mixed acid than cotton cellulose undergoes. Denitration of nitrostarch may be carried out with a very dilute solution of sodium bisulfide. The denitrated starch is freed from sulphur by the treatment with hydrogen peroxide, hot alcohol and hot acetone. Alcohol, acetone-water mixtures, and acetone-alcohol mixtures swell nitrostarch; of these the acetone-water mixtures are the best. The amount of sulphuric acid in the nitrostarch is not more than that in nitrocotton.

<u>1930</u>. Skoglund (35) patented a process for treating nitrated bodies such as nitrostarch. In order to free nitrostarch from residual mixed acid, the latter is displaced by concentrated sulphuric acid. The sulphuric acid saturated nitrostarch is then poured into water giving nitrostarch and a dilute mixture of sulphuric and nitric acids.

In the same year, Pickett (36) patented a method of producing nitrostarch which includes heating starch of normal density to a temperature of 20 to 30°C in the presence of a mixed acid composed of 64 to 67% sulphuric acid, 24 to 18% nitric acid, and 12 to 15% water. He claimed a nitrated starch of relatively low viscosity and a high degree of solubility and stabilization is formed.

In the same year, Berl, Hefter, Rau, Djang and Umstätter (37) made a determination of the molecular weight of nitrated starch by a modification of the method of Barger. They obtained a value corresponding to six to seven anhydroglucose units.

<u>1932</u>. Hackel and Urbanski (38) made a detailed study on the nitration of potato starch by nitric acid as well as mixed acid. In nitrating potato starch with pure nitric acid, the following conclusions are drawn: 1. An increase in the acid concentration causes an increase of the nitrogen content and of the viscosity of the nitrates. 2. Boiling of the nitrates has a detrimental effect including denitration and an increase of their solubilities in alcohol. 3. The nitrogen content increases when the amount of nitric acid used is increased. 4. If the temperature rises above 0°C a lowering of the nitrogen content, of the yield and of the viscosity of the nitrates, accompanied by an increase of alcohol solubility is observed. These changes are probably due to secondary oxidation reactions induced by the rise in temperature. 5. With increasing time of esterification, the nitrogen content of the product rises rapidly at first and then the increase becomes steadily smaller. The increase of the nitration period favours also the above secondary reactions, causing a drop of the yield, of the nitrogen content and of the viscosity of the product. The optimum condition of each variable studied is given in table 4.

Table 4

Optimum variable condition	HNO_3 %	Acid:Starch	Time hrs.	Temp. °C	N %
HNO_3 concentration:					
product stabilized	97.30	10 : 1	2	20	11.73
product unstabilized	97.30	10 : 1	2	20	12.13
Ratio of HNO_3 to Starch	96.26	120 : 1	2	10	13.11
Period of nitration	97.30	10 : 1	24	20	11.96
Temperature of nitration	88.20	10 : 1	2	0	10.00
	97.20	50 : 1	2	0	13.19
Product precipitated by 94.0% H_2SO_4 :					
period of nitration	97.30	10 : 1	6	8	12.58
period of action of H_2SO_4	95.03	10 : 1	4	20	12.67

In nitrating starch with mixed acid, the best yield is obtained with mixtures containing equimolecular quantities of sulphuric acid and water. Such mixtures show a maximum nitrifying power, and behave in the same manner as in the nitration of cellulose. Mixtures poor in sulphuric acid differ in their effect on starch from that on cellulose insofar as nitrated starch is probably soluble in them.

In the same year, Hackel and Urbanski (39) studied the effect of various compositions of mixed acid on different varieties of starches. Different starches nitrated for a period of one hour at 10°C in 50 parts of mixed acid, show no marked differences in nitrogen content, in contradiction of the findings of Berl and Bütler. Their results are given in table 5.

1933. Norman (40) patented a method for producing nitrated porous starch flakes. The method includes subjecting porous starch flakes to the action of a mixture of nitric acid and sulphuric acid, separating the nitrated starch flakes from the acid mixture, washing with water, and finally boiling in an alkaline solution.

Table 5

Mixed acid compn. Balance is H_2SO_4		Percentage of nitrogen in the starch nitrate of					
HNO_3%	H_2O%	Maize	Rice	Corn	Tapicka	Soluble	Potato
20.25	16.55	11.43	11.40	11.42	11.55	11.40	11.52
23.15	11.17	13.02	12.99	13.01	12.97	13.04	13.05
45.17	4.23	13.34	13.30	13.35	13.32	13.27	13.33
43.81	10.50	12.99	12.92	12.91	12.96	12.97	12.97
70.61	4.01	12.77	12.83	12.79	12.85	12.79	12.81
65.56	10.36	12.10	12.11	11.90	12.12	12.08	12.01
98.77	1.23	13.34	13.36	13.20	13.36	13.31	13.33

1935. Kolaczkowska and Urbanski (41) made X-ray photographs of both potato starch nitrate and soluble starch nitrate. Both nitrates show marked resemblances and give the same principal interference rings. Natural potato starch is more crystalline before the introduction of the nitrate groups as compared with the structure of soluble starch. The structure of soluble starch, however, becomes more regular after nitration.

In the same year, Grard (42) moistened starch with 35% of its weight of water and heated it in an autoclave at 150°C for 15 minutes. The resulting plastic mass could be squeezed through a die with a 0.2 mm. opening into long fine threads. These threads of starch, hardens when exposured to air or washed with alcohol. After drying, these threads could be easily powdered and nitrated with 25 parts of nitric acid, 65 parts of sulphuric acid, and 10 parts of water.

In the same year, Berl and Kunze (43) published a paper in which they considered the nitration of starch and the morphology and viscosity of starch nitrates. They nitrated starch under different conditions and found that mixed acid gives a better product than does concentrated nitric acid, and a nitric acid phosphoric acid mixture is even better. The phosphoric acid in the latter case functions like the sulphuric acid in mixed acid and becomes fixed in the resulting product to the extent of 0.19% or more. The esters obtained under these conditions contained 13% nitrogen, whereas the theoretical value is 14.14%. Maximum nitration is effectad in about half an hour.

When completely dry starch is treated with 100% phosphoric acid at 0°C, there is no apparent reaction. Upon the addition of ice cold nitric acid to the mixture, nitration brings almost instantly, and the nitrogen content reaches a maximum in about ten minutes. The resulting product is very stable and has a viscosity much higher than that of the derivative obtained from the action of either concentrated nitric acid or mixed acid on starch. The viscosity of the nitrates of starch is inversely proportional to the extent of the degradation of the molecules. Nitration with mixed acid gives a maximum viscosity after approximately one hour. At the end of twelve hours the viscosity has decreased to about one half of the maximum. A nitric acid phosphoric acid mixture causes much less degradation, as evidenced by the fact that maximum viscosity of the reaction mixture is attained at the end of twelve hours.

X-ray diagrams of the potato starch used show about nine interference rings. This number is reduced to three by nitration, and raised again but not quite up to the original number, when nitrostarch is converted into soluble starch by saponification. Under the microscope, nitrostarch exhibits a transparent shell surrounding on opaque center.

By freezing the moistened nitrostarch, suspending it in water and fractionating it by setting, two products are obtained containing 11.6 and 12.1% of nitrogen. Furthermore, when nitrostarch is treated with acetone the outer shell swells while the inner material dissolves to give a clear solution. This proves the presence of two different materials in nitrostarch, amylose nitrate and amylopectin nitrate. However, seperate nitration of amylose and amylopectin results in products of higher nitrogen content. When starch is heated up to 180°C before nitration in an autoclave the viscosity of the nitrostarch is markedly decreased.

1936. Centola (44) nitrated rice starch with nitric acid of various concentrations, to obtain a series of products containing 8.5 to 12.4% of nitrogen. X-ray examination shows that the nitrostarch with 12.4% nitrogen has a fairly regular structure. Both the positions and intensities of the interference lines resemble those of unstable nitrocellulose containing 12% nitrogen, so that the two substances probably have the same structure. With diminution of the nitrogen content, the diffraction lines become more uncertain, so that the degree of crystallization becomes more imperfect with decrease of the nitro-groups. These esters are constituted of starch molecules with their hydroxyl groups not completely estrified, not of mixtures of unaltered starch molecules and completely estrified ones. This is confirmed by inability to fractionate these mixtures with any solvent.

Eight samples of rice starch are immersed in a mixed acid having the composition: nitric acid 41 parts, sulphuric acid 56 parts, and water 3 parts; at 20°C for periods of 3 to 200 minutes. After washing with water and 70% alcohol, the products contain 11.0 to 13.3% of nitrogen. They all give diffraction spectra of nitrostarch, even those subjected to the mixed acid the shortest times, where unaltered starch is also recovered.

Though nitrostarch prepared from nitric acid gives clear solutions in methanol, that prepared from mixed acid is found only to be partially soluble. The insoluble material is removed by filteration and the soluble portion precipitated with water. Both substances show the same X-ray diagram. That portion insoluble in methanol is termed amylopectin nitrate because saponification by the method of Damansky yields amylopectin; that portion soluble in methanol is termed amylose nitrate because saponification gives amylose. Nitrostarch containing 12.45% nitrogen gives an amylose nitrate containing 12.50% nitrogen and an amylopectin nitrate containing 12.34% nitrogen. This behaviour is in harmony with the fact that the nitration of amylose gives an amylose nitrate identical with that obtained from the methanol soluble portion of nitrostarch and from nitrostarch prepared from nitric acid alone. This explains why nitrostarch prepared from nitric acid is soluble in methenol and gives a less sharp X-ray diagram than does that prepared from mixed acid. The differences between the two fractions of nitrostarch are the same as those between amylose and amylopectin, i.e. a different degree of polymerization and crystallization. Potato starch and been starch give nitrostarch with the same properties as that from rice, so that the structural differences in the various types of starch disappear in the transformation to nitrostarch.

In the same year, Staudinger and Eilers (45) studied the effect of nitration by mixed acid on the molecular weight of starch. They found that the nitrates of starches of high molecular weight have lower molecular weights than the nitrates of starches of low molecular weight. They concluded that the destruction of the alpha glucosidal linkage of starch molecule must take place before nitration.

1937. Urbanski and Janiszewski (46) examined the nitrating action of nitric anhydride on starch and cellulose. Starch nitrated with gaseous nitric anhydride or with nitric acid containing nitric anhydride contains up to 13.85% nitrogen.

1938. Nitrokémia Ipartelepek r.t. (47) patented a process comprising the treatment of starch powder with four to six parts by weight of an acid mixture containing 75 to 85% nitric acid and 25 to 15% sulphuric acid. During the mixing and subsequent reaction, the temperature of the material is maintained below 5°C.

The nitrating acid is removed from the nitrated starch by displacement of the acid with water. This is accompolished by drawing the water successively through a series of batches of the nitrated starch on filters where in the liquid drawn through the last filter of the series is passed into the next preceeding filter and so on, until the acid from the successively filtered batches of the series is drawn through a filter containing fresh nitrated starch. The water washed nitrated starch is withdrawn from that end of the series where the fresh water enteres, while the filter thus cleared before being charged again with nitrated starch is freed from water. The nitrostarch is then pressed in vacuo to remove most of the water, and the mass is disintegrated and dried by an air current.

1945. Berl (48) patented a process for the nitration of alcohols similar to starch. Starch can be nitrated in a few seconds or minutes to a compound containing 13.95% nitrogen by means of a mixture of phosphorus pentoxide, metaphosphoric, and nitric acids. The nitric acid which constitutes 50 to 60% of the mixture is reduced to a few tenths of a percent during the nitration.

Mixed acid containing acetic acid and acetic anhydride instead of metaphosphoric acid and phosphorus pentoxide is also suitable and gives equally good results. A mixed acid which is composed of phosphorus pentoxide, nitric, metaphosphoric, and acetic acids can also be used.

1946. Caesar (49) patented a process for anhydrous nitration of organic compounds. In the nitration process, water is formed which dilutes the nitrating mixture and hinders the reaction. If nitrogen pentoxide is used, then nitric acid, instead of water, is formed, and by nitrating with dinitrogen pentoxide in the presence of phosphorus pentoxide, the latter reconverts the formed nitric acid back to the reagent.

$$2\,HNO_3 + P_2O_5 = N_2O_5 + 2\,HPO_3$$

A non-aqueous inert solvent such as chloroform, carbon tetrachloride, or propylene dichloride is used. Since water is not present, there is no degradation of the starch molecules and no reduction in viscosity. Since sulphuric acid is not used, no sulphates which are difficult to remove from the nitrated starch are formed.

In the same year, Caesar and Goldfrank (50) described in detail a laboratory method and apparatus for the preparation of dinitrogen pentoxide and the nitration of starches. The nitration is carried out in chloroform or any suitable non-aqueous solvent. A simple and effective means of removing the nitric acid, which is produced as a by product in the nitration, is the use of sodium fluoride which probably forms a hydrogen bonded complex as NaF.HO-NO_2. In this way the by product nitric acid is not allowed to react with the starch to produce water, whence, the efficiency of the nitration reaction is greatly increased. Owing to the completely anhydrous character of the nitration, and the relatively low temperatures involved the nitric esters produced are considered to reflect the degree of polymerization of the parent material. A brief summary of their results is given in table 6.

Table 6

Conditions	Gm. N_2O_5: starch	Gm. N_2O_5: 100 ml.	Time min.	Temp. °C	% N
Corn starch	4.3	14.5	30	10	13.98
Corn starch	3.9	12.8	20		13.93
Corn starch	3.2	16.3	25	10	13.89
Corn starch	4.4	14.6	20		13.92
Corn amylose	3.9	10.8	20	5	13.96
Corn amylopectin	4.6	15.4	20	10	13.98
Potato starch	4.6	15.2	60	2	11.33
Potato starch	3.9	13.0	64	16	13.92
Potato starch	4.4	14.7	60	12	13.89
Potato amylose	5.7	14.3	20	10	13.2
Potato amylopectin	4.7	14.3	20	9	12.8

1947. Ashford and Hibbert (51) studied the effect of hot alkali on the nitrates of starch, amylose, and amylopectin. This reagent is found not to cause appreciable denitration, nor does it result in a useful stable nitrate.

1951. Brissaud and Ronssin (52) described the work done at "Laboratoire Central des Poudres" on the preparation of starch nitrates. Starch is nitrated by a mixture of equal parts of nitric acid and acetic acid mixed with acetic anhydride. The product is precipitated with cold water to give a nitrate of starch containing 10.2% nitrogen. When the reaction is carried out in chloroform, the product contains up to 14.11% nitrogen. Most of the previous work on the preparation of starch nitrates is also verified under more or less identical conditions.

In the same year, Vollmert (53) found that starch swells strongly in mixtures of nitric and sulphuric or nitric and phosphoric acid, making the product difficult to separate. Starch can be nitrated with dinitrogen pentoxide but the latter is difficult to prepare and preserve. Thus, he described a method whereby dinitrogen pentoxide is distilled under high vacuum directly from a phosphorus pentoxide-nitric acid mixture onto the sample. After the reaction is complete, the nitrogen pentoxide is distilled back to the original flask. The apparatus consists of two flasks connected together, and distillation from one flask to the other is carried out by immersing one in a freezing mixture. Nitration by this procedure gives starch nitrates containing between 9.7 and 10.0% nitrogen. It is also shown that by the nitration under the described conditions no degradation of the chain occurs.

B. EXPERIMENTAL

2. Estimation of nitrogen

The methods employed for the estimation of nitrogen in substances containing it are numerous. Most of these methods are applicable to explosive compounds, especially those of the nitrate ester type.

The Dumas' method consists in combusting the organic compound in the presence of copper oxide in an atmosphere of carbon dioxide and passing the gases evolved over heated copper oxide or lead chromate and metallic copper. The last portions of the nitrogen produced are displaced with carbon dioxide, and collected over a strong caustic soda solution, which absorbs the carbon dioxide.

The nitron method consists in saponifying the nitrate ester by boiling with caustic soda, to which some hydrogen peroxide has been added to prevent reduction. The solution is then diluted, acidified with sulphuric acid, and the nitric acid is precipitated with acetat of nitron. Cope (54) reported comparative determinations of the nitrogen of starch nitrate by the use of the nitrometer and the nitron methods. He found that the nitrogen content in a sample of starch nitrate determined by the nitrometer method is 13.00%; while by the nitron method it is 13.04%. From these results he concluded that the use of the simple nitron method is satisfactory for the determination of nitrogen in the nitrostarch.

The method published by Kesseler, Röhm and Lutz (55) for the determination of nitrogen in nitric acid esters, as for example nitrostarch, consists of saponifying the ester, followed by reduction in an alkaline solution. The ammonia formed is then distilled into a known quantity of acid.

2.1 The nitrometer method (du Pont type) (56)

2.1.1 Principle

The determination of nitrogen in nitrates by use of the nitrometer depends upon the decomposition of the nitrate by sulphuric acid in the presence of mercury and the quantitative liberation of nitric oxide, according to the following equation:

$$2\ RNO_3 + 4\ H_2SO_4 + 3\ Hg = R_2SO_4 + 3\ HgSO_4 + 4\ H_2O + 2\ NO.$$

This reaction is applicable to the du Pont nitrometer, as well as to all nitrometers of the Lunge type.

2.1.2 Description of the du Pont nitrometer

The essential glass parts of the du Pont nitrometer illustrated in figure 9, consist of a reaction bulb A, a compensating tube B, a measuring tube C, and two mercury reservoires D and E. These glass parts are connected together in two units, one unit consisting of the reaction bulb and a mercury reservoir joined by a section of special rubber tubing, and the other unit consisting of the measuring tube, the compensating tube, and a mercury reservoir each connected to one nipple of a three-way manifold by sections of rubber tubing. The reaction bulb and the measuring tube are connected together by a ball and socket glass joint.

The distinguishing feature of the du Pont nitrometer is the compensating device, whereby the volume of NO is always read under standard conditions, thus avoiding the observation of atmospheric pressure and temperature and subsequent calculation. The compensating tube is filled with dry air, or preferably dry nitrogen, which at 20°C and a pressure of 760 mm. occupies a definite volume (indicated by a mark on the tube), so that by bringing the mercury level to the mark on the compensating tube, and that in the gas measuring tube to the same level, the gas to be measured occupies the same volume it would have at 20°C and 760 mm.

The measuring tube of the nitrocotton type, designed espesially for the determination of nitrogen in nitrocellulose, nitrostarch, and similar substances where the results are to be expressed in percent of nitrogen, consists of a bulb with a cylindrical extension graduated from 10.00 to 14.01. The graduations are such that if a sample of exactly 1.0000 gram is taken and the volume of gas observed at 20°C and 760 mm., the reading on the tube will give the correct percentage of nitrogen in the sample directly. The volume of the tube at the 14.01 mark is made equal to 240.36 ml. at 20°C and 760 mm. Since the mass of 240.36 ml. of NO gas, under standard conditions, is 0.3001 gram, the mass of the nitrogen which is equivalent to this volume of NO is 0.1401 gram. In other words, the tube full of gas (14.01 units) contains 0.1401 gram of nitrogen. Therefore, each whole unit corresponds to 0.01 gram of nitrogen, or when a 1 gram sample is taken to 1.0%.

Since the capacity of the nitrocotton tube is 240.36 ml., each major graduation corresponds to 17.156 ml., and the gas required to fill the tube to the 10.00 mark must, therefore, occupy 171.56 ml. This makes it necessary to adjust the size of the sample so that the volume of the gas falls between 171.56 and 240.36 ml. under standard conditions.

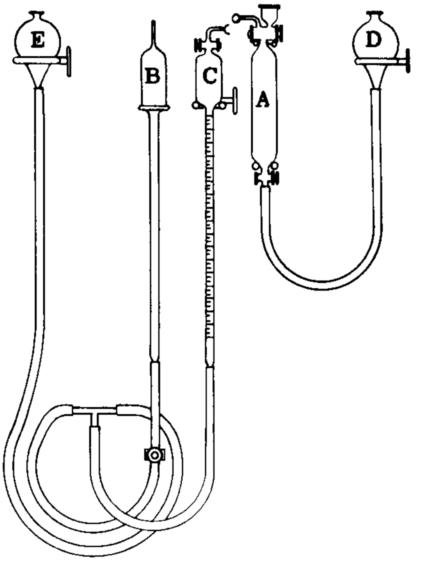


Figure 9 The du Pont nitrometer

2.1.3 Standardization against standard potassium nitrate

A sample of approximately 0.95 gram of analytical grade potassium nitrate, dried at 140 to 150°C for three hours and cooled in a desiccator is weighed into a 15 cc., tared weighing bottle. Drying is then repeated for additional periods until the sample is brought to constant weight.

The reaction bulb is prepared for the reception of the sample by shaking the mercury with 25 ml. of 95% sulphuric acid. The lower stopcock is opened the upper two-way stopcock turned to communicate with the exit tube. The socket at the end of the capillary is then closed with a tightly fitting ground glass ball. The two-way stopcock is turned to communicate with the capillary throat of the cup until the bore of the stopcock is just filled with mercury. Approximately 10 ml. of distilled water are poured into the cup, drawn into the reaction bulb and then run back into the cup by raising the reservoir. This wash water is then removed from the cup with tissue paper. The reservoir is lowered so that the mercury level is about 2 cm. below the throat of the cup. The reaction bulb is now free from acid in the cup or capillary and ready to receive the sample.

The bottle with sample of potassium nitrate are weighed accurately and the contents tipped into the cup of the reaction bulb, thus removing most of the sample. The bottle is weighed and the weight of potassium nitrate is calculated. Then 1.5 ml. of water are added and the mixture stirred in the cup with a short, pointed galss rod to remove air bubbles. The undissolved crystals are worked out into the lower part of the cup, keeping them below the surface of the solution. THE LOWER STOPCOCK IS OPENED, and the mixture is introduced into the bulb by opening the upper stopcock very slightly. The stopcock is very quickly turned all the way over and back, thus drawing practically all the crystals into the bulb. The remaining solution slowly added and the cup rinsed out with a second portion of 1.5 ml. water, to dissolve all remaining particles of nitrate in the cup.

The cup is finally washed five or six times with a total volume of 25 ml. of 95% sulphuric acid. The first of these wash portions is added carefully to the water solution of potassium nitrate in the reaction bulb, so that the sudden generation of heat will not cause a pressure sufficient to force some of the solution back into the cup with consequent loss of nitric acid. A slight suction is always maintained when introducing the sample, wash water, and acid, care is being taken not to draw any air into the reaction bulb. Finally, the cup is wiped free from adhering acid with tissue paper.

The reservoir is lowered on the rack and the bulb removed from its support. The bulb is held in a vertical position, not more than 15 cm. above the reservoir, and slowly shaken with a lateral motion until the reaction starts, care being taken not to allow the acid nor the sample to swirl down out of the bulb into the rubber tube. As the reaction proceeds, the mercury is allowed to run out of the bulb to about 3 cm. above the lower stopcock. After the preliminary decomposition is complete, the lower stopcock of the reaction bulb is closed, the bulb elevated about 10 cm. above the mercury level in the reservoir, and given two or three vigorous shakes. The lower cock is opened immediately and the bulb placed beside the reservoir in such a position so that the mercury in the reaction bulb is about 5 cm. above the level of the mercury in the reservoir. The lower stopcock is closed, the reaction bulb shaken two or three times, and the comparison repeated. This procedure is continued until the decomposition is apparently complete. With both stopcocks closed, the bulb is shaken vigorously for at least three minutes, after which it is placed on the rack.

The gas is transferred to the measuring tube, the compensating tube clamped off, the measuring tube lowered as far as possible on the stand and, a little mercury forced out of the capillary of the measuring tube by raising the reservoir, being caught in a beaker. The reservoir is lowered to about half way down its supporting rod and the measuring tube raised until both the ball and socket of the ground joint are at the same level. The glass ball is removed cautiously and the ball and socket connected tightly, care being taken not to trap any air in the capillary.

The lower stopcock of the reaction bulb and the stopcock of the measuring tube are opened, and the upper stopcock of the reaction bulb is turned to allow the gas to pass into the measuring tube. The right hand reservoir is raised well above the cup and the speed of flow of the gas controlled by the stopcock on the measuring tube. The last portion of the gas is run from the reaction bulb quite slowly to avoid acid from entering the measuring tube. When the acid has just filled the capillary of the measuring tube, its stopcock and the upper stopcock on the reaction bulb are closed and the clamp from the ball and socket joint removed. The measuring tube is raised until the gas is approximately at atmospheric pressure and allowed to cool for 20 minutes. The weight of the gas that should be evolved from the weight of the sample is calculated as follows:

$$\frac{14.01 \text{ x wt. of sample}}{1.0111} = \text{Reading}$$

The mercury columns in the compensating and measuring tubes are adjusted to about the same level at the calculated reading on the measuring tube. A narrow strip of gummed label is pasted vertically on the compensating tube with its center approximately at the determined level. The columns are carefully adjusted until exactly correct, that is, the mercury in the two tubes is brought to exactly the same level by means of the small levelling tube with the aid of a mirror. The reading on the measuring tube should be exactly as calculated above. When these conditions have been obtained, a narrow pencil mark is made on the label at the top of the mercury meniscus.

The determination is repeated on another portion of potassium nitrate but this time the mercury is adjusted in the compensating tube to the pencil mark and the mercury in the measuring tube brought exactly to the level of the mark on the compensating tube. The volume of gas is then read under these conditions and the percentage of potassium nitrate is calculated as follows:

$$\frac{\text{Corrected reading x 1.0111}}{\text{wt. of sample}} = \%\ KNO_3$$

If the mark has been set correctly in the first standardization, check determinations should give 100.00% $KNO_3 \pm 0.10\%$ and should not vary more than 0.05% from each other. At least two check determinations should be made after setting a new mark. If either show too great a variation from 100% the levels should be readjusted and a second mark made before the gas is expelled from the measuring tube. The standardization is repeated until the correct mark is thoroughly established. By this procedure, the volume of gas in the compensating tube is made to correct for temperature, pressure, solubility of NO in acid, and in fact all conditions of operation.

After each determination, the sulphate sludge and acid residue are expelled from the reaction bulb. Then, with the reaction bulb in its normal position on the rack and the bottom stopcock opened, about 25 ml. of 95% acid are introduced into the bulb by pouring it into the cup, opening the twoway stopcock, and lowering the reservoir. About one third of the mercury is allowed to run back into the reservoir, the bottom stopcock is closed, and the bulb shaken vigorously until all the solid matter and sludge have been freed from its surface. Then, the washing acid is discharged in the regular manner. It is not necessary to remove every trace of acid from the bulb, but every trace of acid must be washed out of the cup and the cup dried before proceeding with another determination. The NO gas is expelled from the measuring tube into the fume line by lowering the tube and raising the reservoir. During this operation it is well to close the clamp on the compensating tube to prevent a sudden change of pressure therein.

2.1.4 Analysis of starch nitrates

Samples of approximately 1 gram nitrostarch dried at 45°C for 2/3 days are transferred into the cup, and 25 ml. of nitrogen-free 95% sulphuric acid are added in small portions until a sufficient quantity has been added to make an emulsion with the nitrostarch. The rest of the operating procedure is identical with that previously described under standardization.

The percentage of nitrogen in any starch nitrate is given by:

$$\frac{\text{Corrected reading}}{\text{wt. of sample}} = \%\,\text{N}$$

2.2 The Bowman and Scott method (57)

This method involves the titration of nitrates with ferrous sulphate and is as easy and quick as any ordinary titration. It has a wide range of usefulness and is accurate enough for most purposes.

2.2.1 Principle

In the presence of sulphuric acid, nitrates are reduced not to NO, but to N_2O_3. Strong heating will, however, drive the reaction somewhat further. The reaction that occures in the cold is, therefore:

$$4\,FeSO_4 + 2\,HNO_3 + 2\,H_2SO_4 = N_2O_3 + 2\,Fe_2(SO_4)_3 + 3\,H_2O.$$

The end point is a delicate pinkish brown.

Water slows down the reaction and weakens the color of the end point, so that a considerable excess of ferrous sulphate is required to give a readable tint. Larger quantities of water stop the reaction entirely in the cold. As a maximum 25% of water is permissible, though it makes a rather difficult end point.

The temperature of titration should be low. Too high a temperature acts in two opposite ways: (a) it causes volatilization of nitric acid, which leads to low results; (b) it causes a slight reduction of N_2O_3 to NO, which results in higher values. Thus the temperature should be kept as low as possible and should in no case exceed 60^oC.

Ferrous sulphate attacks N_2O_3 slowly under the conditions of the titration, but it has so marked a preference for nitric acid that reduction of N_2O_3 does not occur to any extent while nitric acid is present. Since the brown color of the end point is due to the formation of a compound of ferrous sulphate with NO, some slight reduction to NO must always occur. A 0.2 ml. excess of ferrous sulphate solution (1 ml. = 0.02 gram HNO_3) is required to give the brown tint of the end point in a volume of 100 to 150 ml.

2.2.2 Titration of starch nitrate with ferrous sulphate

Based on the foregoing discussion, the following standard procedure is recommended for analysis of starch nitrate with concentrated sulphuric acid as a medium.

The ferrous sulphate solution is prepared by dissolving 176.5 grams of analytical grade $FeSO_4.7H_2O$ in 400 ml. water. A volume of 500 ml. of sulphuric acid made by mixing equal volumes of water and the concentrated acid is added gradually to this solution with stirring. The mixture is cooled and made up to one liter.

The iron solution is standardized in the following manner. One ml. of 0.45 normal nitric acid is delivered slowly from a pipette to the bottom of a conical flask containing 25 ml. of concentrated sulphuric acid and standing in a dish containing ice water. The iron solution is run in slowly from an automatic burette with constant stirring until the solution becomes faint brown or pink. Then, the pipette is rinsed by drawing the solution into it and allowing it to drain and the titration is completed. The volume of the iron solution required to effect the color change is negligible in comparison with the volumetric error under the conditions of titration. The strength of the iron solution is given by:

$$1 \text{ ml. } FeSO_4 = \frac{1}{1000} \times \frac{0.45 \times 14}{\text{Vol. of } FeSO_4} \text{ grams nitrogen}$$

Approxomately 50 milligram samples of nitrostarch dried at 45°C for three days are transferred to 200 cc. conical flasks and 25 ml. of nitrogen-free concentrated sulphuric acid added. After allowing to stand for five minutes the samples are titrated as described above.

2.3 Tolerances in the results of analysis of starch nitrates

Repeated analyses of the same substance, do not always give exactly the same numerical results. It is even more difficult to take two or more samples of an explosive substance, which is liable to spontaneous decomposition, and obtain identical values. The extent to which the analysis or sample may differ will vary with the analytical method employed, and the character of the substance analyzed.

During the preparation of the starch nitrates under different conditions, great care is taken to obtain as homogeneous a products as possible. Furthermore, since starch nitrates are liable to spontaneous decomposition at elevated temperatures or to hydrolysis in presence of excessive amounts of moisture, the samples are carefully dried at 45°C for two days.

The Bowman and Scott volumetric method is employed for the determination of nitrogen throughout this work. A number of analyses are cross-checked by the du Pont nitrometer as well as the Dumas methods. The tolerences in the results of the three above mentioned methods are given for comparison in table 7.

Table 7

Method	Amylose nitrates			Amylopectin nitrates		
du Pont nitrometer	11.38	12.20	13.82	11.42	12.40	13.48
Dumas	11.38	12.11	13.80	11.47	12.44	13.42
Bowman and Scott	11.42	12.30	13.86	11.50	12.50	13.52

3. Nitration of starch fractions

3.1 Mathematical relations

It is apparent that the starch molecules contain three hydroxyl groups per anhydroglucose unit. Thus, the nitration of the starch molecules of the empirical composition $C_6H_7O_2(OH)_3$ gives a series of nitration products as shown in table 8.

Table 8

Characteristics	Starch nitration products		
	mononitrate	dinitrate	trinitrate
Empirical composition	$C_6H_7O_2(OH)_2ONO_2$	$C_6H_7O_2(OH)(ONO_2)_2$	$C_6H_7O_2(ONO_2)_3$
No. of ONO2 grs. per anhydroglucose unit	1	2	3
Nitrogen content %	6.76	11.11	14.14
Increase in weight of starch %	27.7·	55.5·	83.3·
Oxygen balance	-73.5	-44.5	-24.2

An absolutely complete nitration corresponding to the trinitrate is difficult to obtain. If the conditions of nitration are less severe, less nitrogen is introduced, and products ranging several per cent of nitrogen upward and differing widely in physical and explosive properties may result.

In the starch nitrates which contain less than enough nitrogen to correspond to the trinitrate, the nitrate groups are believed to be distributed at random among the three possible positions and no definite structural formulas can be assigned to the substances. Nor is it to be supposed that a sample which may correspond in empirical composition to starch mononitrate or dinitrate really represents a single chemical compound.

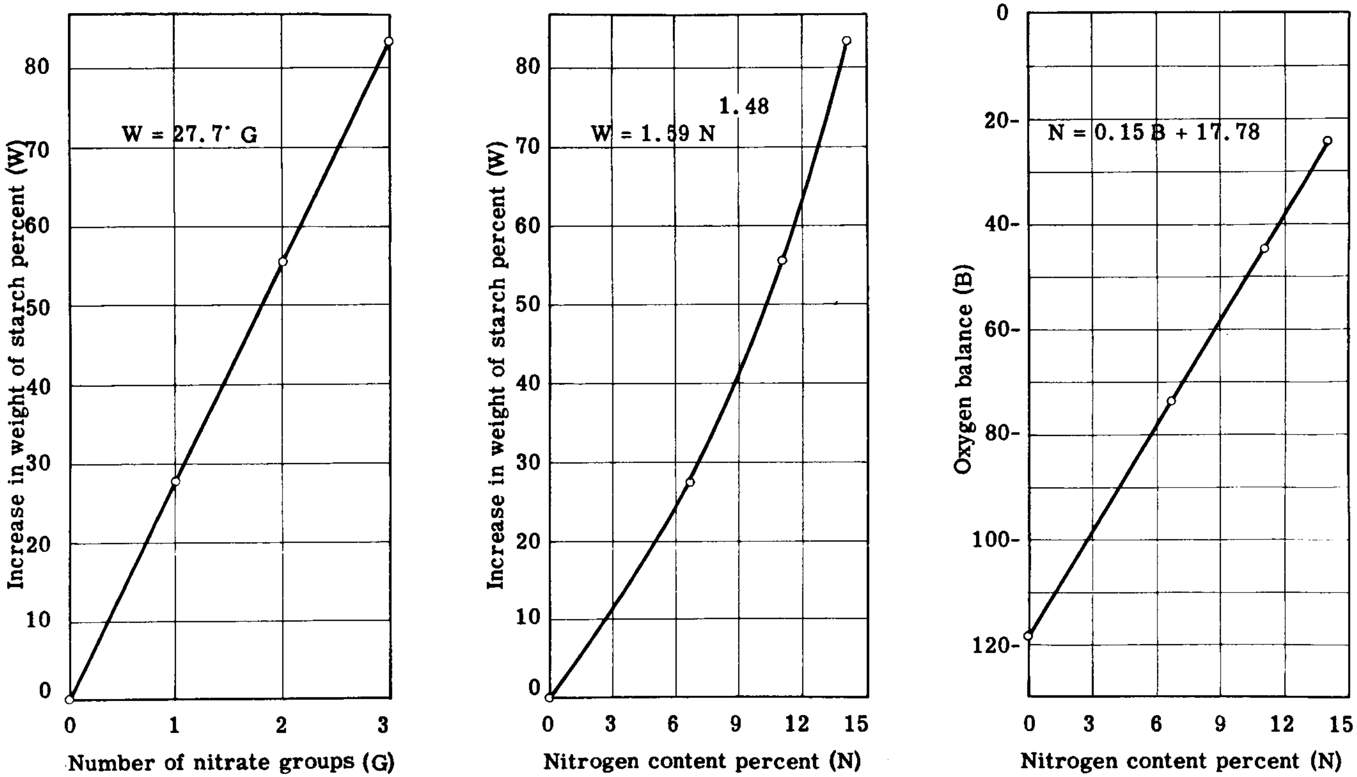


Figure 10 Mathematical relations accompanying starch nitration

However, the changes accompanying nitration follow definite mathematical relations. As derived by Bishara (58), the relation between the percentage increase in weight of starch (W) and the number of entering nitrate groups per anhydroglucose unit (G) is linear and may be represented by the equation of the first degree

$$W = 27.7 \cdot G$$

Furthermore, the relation between the percentage increase in weight of starch (W) and the nitrogen content per cent of starch nitrate (N) is parabolic and may be represented by the equation of the 1.48 degree

$$W = 10^{0.2} N^{1.48}$$

Finally, the relation between the nitrogen content percent of starch nitrate (N) and the oxygen balance (B) is linear and may be represented by the equation of the first degree

$$N = 0.15 B + 17.78$$

The oxygen balance is given by

$$B = \frac{1600 (z - 2x - 1/2y)}{\text{Molecular weight}}$$

where x, y, and z represent the numbers of atoms of carbon, hydrogen, and oxygen per glucose residue. These relations are graphically represented in figure 10 and can be utilized to solve the mathematical relations following starch nitration.

3.2 Nitration of amylose with nitric acid in the presence of acetic anhydride

The nitration of starch or its components with nitric acid in the presence of acetic anhydride has not been previously attempted. The use of a mixture of nitric acid and acetic acid, to which acetic anhydride is added, has been mentioned in the literature; but no attempt has been made to study the nitration parameters in detail. Thus, a comprehensive study was undertaken to evaluate the effects on the degree of nitration of amylose, arising from the change of temperature and period of nitration, as well as medium composition.

The effect of temperature on the degree of nitration is studied at 10, 20 and 30°C, while that of the nitration period is measured after 3, 6, 12 and 24 hours. The effect of medium composition on the degree of nitration is studied at 10, 20, 30, 40, 50, and 60 per cent by volume of acetic anhydride to nitric acid of specific gravity 1.5. Higher percentages of acetic anhydride slow down the esterification reactions, and make the nitrated product very difficult to filter. The ratio of amylose to the nitric acid acetic anhydride mixtures is varied between 1:10, 1:25, and 1:50, while lower ratios prevent the formation of a homogeneous medium.

3.2.1 Nitration apparatus

The nitration appratus illustrated in figure 11 consists of a double walled nitration flask G having four ground joints. The central ground joint is equipped with a "Jena KPG well" D containing a "Jena stirrer" F driven by an electric motor A. A thermometer E, graduated in 0.5 of a degree, is fitted to a second ground joint next to the central one. A third ground joint, next to the central one, is fitted with a dropping funnel C which can be removed and displaced by a sample taking device H. The latter consists of inlet and outlet tubes fused to a ground stopper to which a small round flask is fitted by means of hooks and spring attachments. The fourth ground joint is fused to a side tube permitting attachment of a ground joint reflux condenser B. The temperature is regulated by circulating water through the jacket by means of a forced circulation thermostat I.

3.2.2 Detailed procedure of nitration

Samples of 5, 10 or 25 grams of amylose dried at 100°C for two hours are introduced into the nitration flask and multiples of 25 ml. up to 150 ml. of acetic anhydride, according to the medium composition, are added from the dropping funnel. During the addition, a fast stream of cold tap water (6-8°C) is passed through the jacket. Appropriate volumes of nitric acid of specific gravity 1.5 to make 250 ml. with the volume of acetic anhydride added are cooled to -10°C, and then added from the dropping funnel in a fine stream with vigorous stirring. During the addition, which required approximately 10 minutes, the temperature is not allowed to rise more than 5°C above the operating temperatures 10, 20,

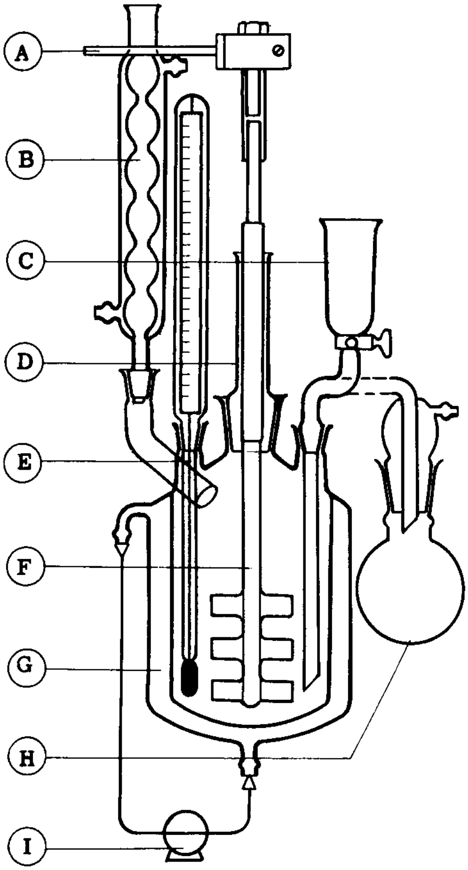


Figure 11 Nitration apparatus

and 30°C. After the nitric acid have been added, the jacket is connected to the circulating thermostat and the temperature adjusted precisely to the operating figure. The dropping funnel is then replaced by the sample taking device and samples of about 60 ml. withdrawn from the reaction mixture at intervals of 3, 6, 12, and 24 hours. As the samples are withdrawn, they are immediately poured into one liter of ice cold deionized water. The precipitated amylose nitrate is separated by filteration through a sintered glass funnel, washed in one liter of 1% ammonia solution and filtered again. It is then boiled for one hour in one liter of deionized water, filtered, and this boiling procedure repeated four times with fresh amounts of deionized water. After the final filteration, the mass is dried at 40 to 45°C for three days.

The different preparations of amylose nitrates are analyzed for nitrogen by the Bowman and Scott method.

3.2.3 Results of nitration

The results in tables 9 to 17 which are graphically shown in figures 12 to 20 show the effect of reaction period and medium composition on the degree of nitration of amylose, when other parameters are kept constant according to the following classification:

Table	Figure	Amylose-medium ratio	Temperature
9	12	1 : 10	10
10	13	1 : 10	20
11	14	1 : 10	30
12	15	1 : 25	10
13	16	1 : 25	20
14	17	1 : 25	30
15	18	1 : 50	10
16	19	1 : 50	20
17	20	1 : 50	30

Figures 21, 22, 23, and 24 show the effect of temperature and medium composition on the degree of nitration of amylose after 3, 6, 12, and 24 hours respectively when the amylose medium ratio = 1 : 25

Table 9

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:10, Temperature $10^{\circ}C$

Medium composition by vol.	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.08	11.55	11.91	12.20	12.49	12.33
N content % After 6 hours		11.33	11.70	12.11	12.55	12.66	12.49
N content % After 12 hours		11.67	12.07	12.57	12.84	12.98	12.65
N content % After 24 hours		12.31	12.67	13.07	13.36	13.33	13.02

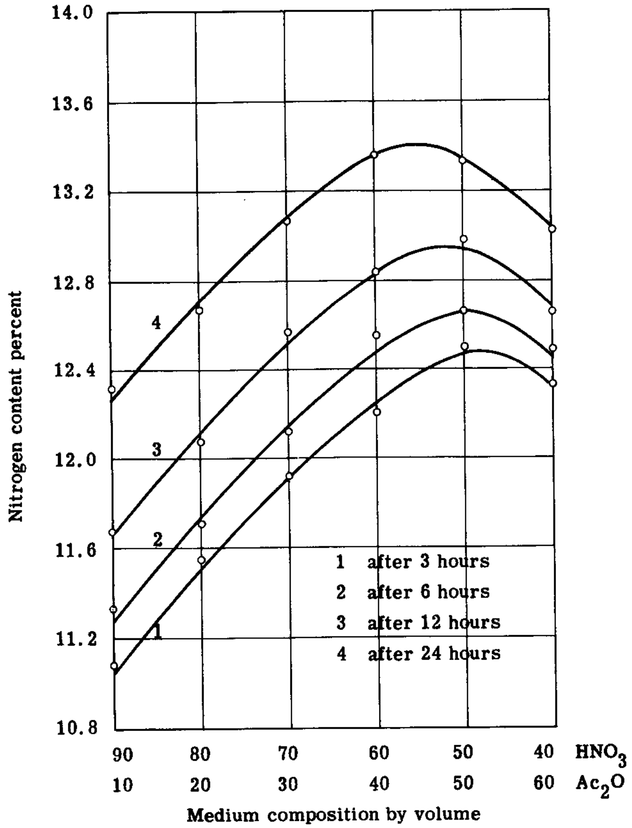


Figure 12

Table 10

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:10, Temperature 20°C

Medium composition by vol.	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.14	11.56	12.11	12.35	12.59	12.34
N content % After 6 hours		11.34	11.98	12.44	12.71	12.87	12.52
N content % After 12 hours		11.73	12.50	12.99	13.43	13.28	12.78
N content % After 24 hours		12.66	12.97	13.40	13.54	13.50	13.12

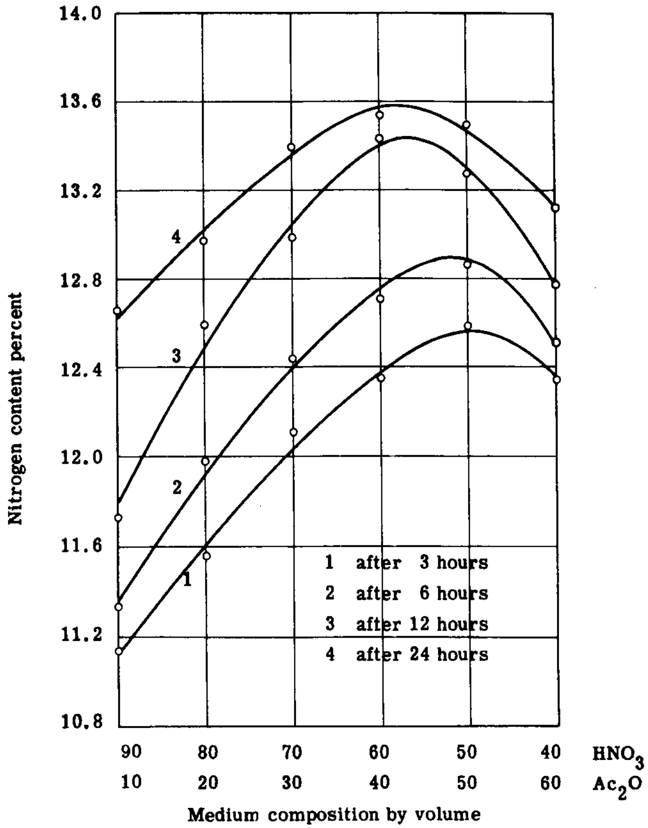


Figure 13

Table 11

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:10, Temperature 30°C

Medium composition by vol.	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.18	11.83	12.42	12.82	12.88	12.36
N content % After 6 hours		11.55	12.20	12.92	13.41	13.30	12.70
N content % After 12 hours		12.00	12.91	13.60	13.84	13.53	13.00
N content % After 24 hours		12.95	13.17	13.48	13.66	13.62	13.28

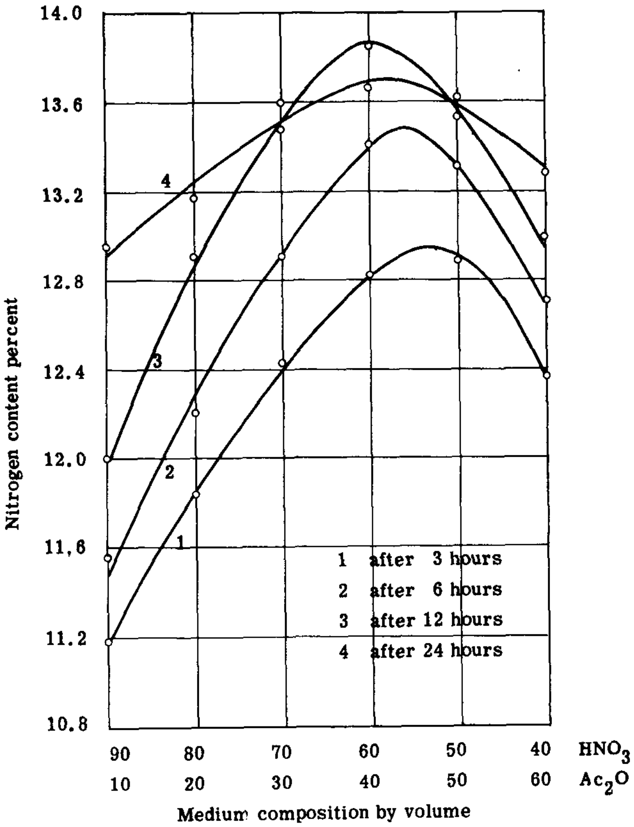


Figure 14

Table 12

Effect of reaction period and medium composition on the degree of nitration of amylose Amylose-medium ratio = 1:25, Temperature 10°C

Medium composition by vol.							
	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.12	11.50	11.91	12.37	12.56	12.35
N content % After 6 hours		11.40	11.74	12.20	12.57	12.69	12.50
N content % After 12 hours		11.72	12.21	12.52	12.95	13.04	12.69
N content % After 24 hours		12.47	12.80	13.06	13.46	13.50	13.06

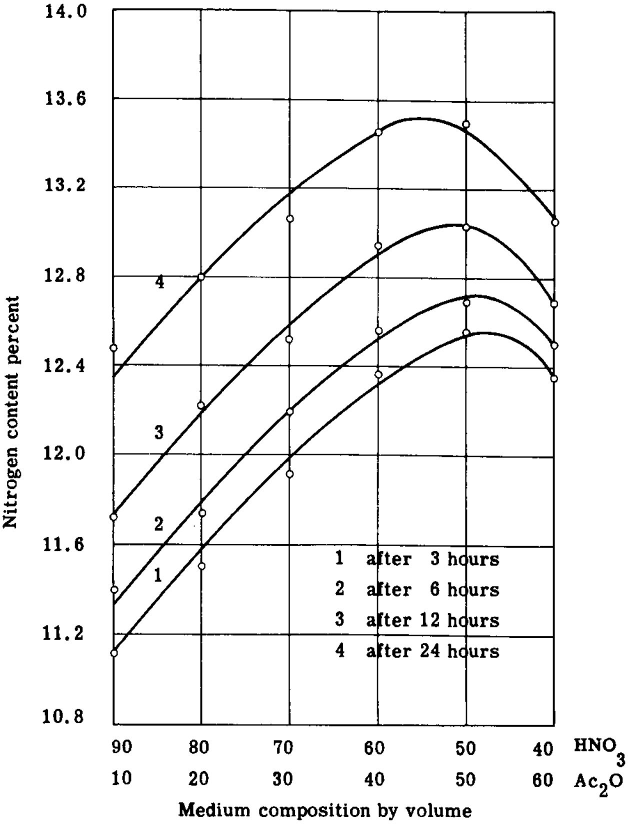


Figure 15

Table 13

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:25, Temperature 20°C

Medium composition by vol.							
	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.20	11.77	12.03	12.46	12.68	12.38
N content % After 6 hours		11.48	12.09	12.39	12.95	13.04	12.54
N content % After 12 hours		11.89	12.67	13.12	13.61	13.45	12.81
N content % After 24 hours		12.72	13.16	13.40	13.68	13.58	13.11

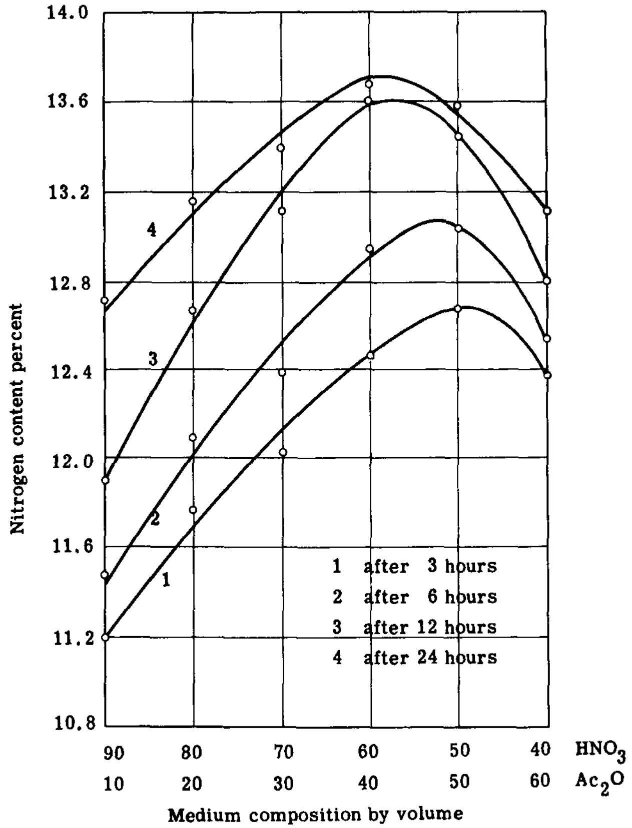


Figure 16

Table 14

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:25, Temperature 30°C

Medium composition by vol.	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.23	12.00	12.47	12.90	13.05	12.42
N content % After 6 hours		11.57	12.52	12.98	13.57	13.40	12.71
N content % After 12 hours		12.06	12.89	13.68	13.96	13.61	12.95
N content % After 24 hours		13.00	13.35	13.55	13.76	13.71	13.31

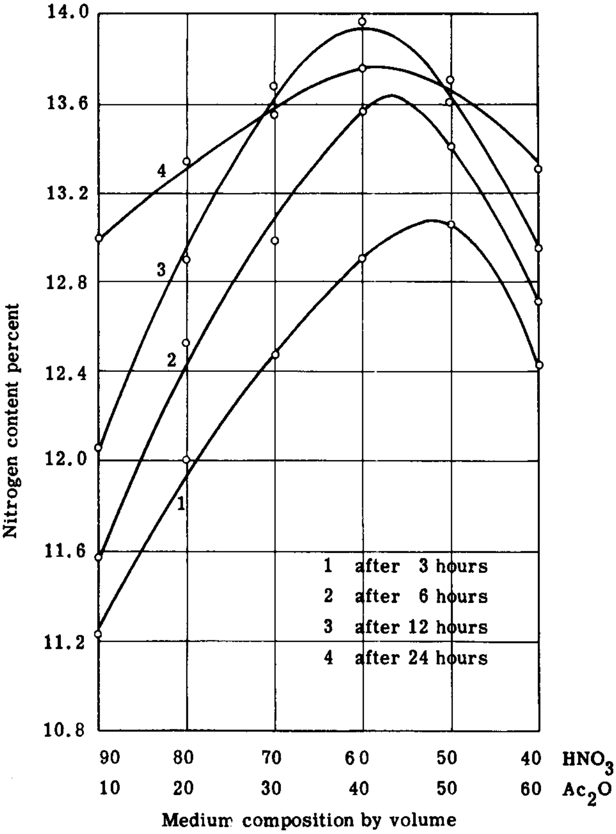


Figure 17

Table 15

Effect of reaction period and medium composition on the degrce of nitration of amylose

Amylose-medium ratio = 1:50, Temperature 10^{o}C

Medium composition by vol.	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.20	11.61	12.10	12.37	12.59	12.40
N content % After 6 hours		11.46	11.86	12.20	12.57	12.78	12.53
N content % After 12 hours		11.86	12.23	12.59	13.06	13.08	12.75
N content % After 24 hours		12.47	12.82	13.19	13.59	13.51	13.13

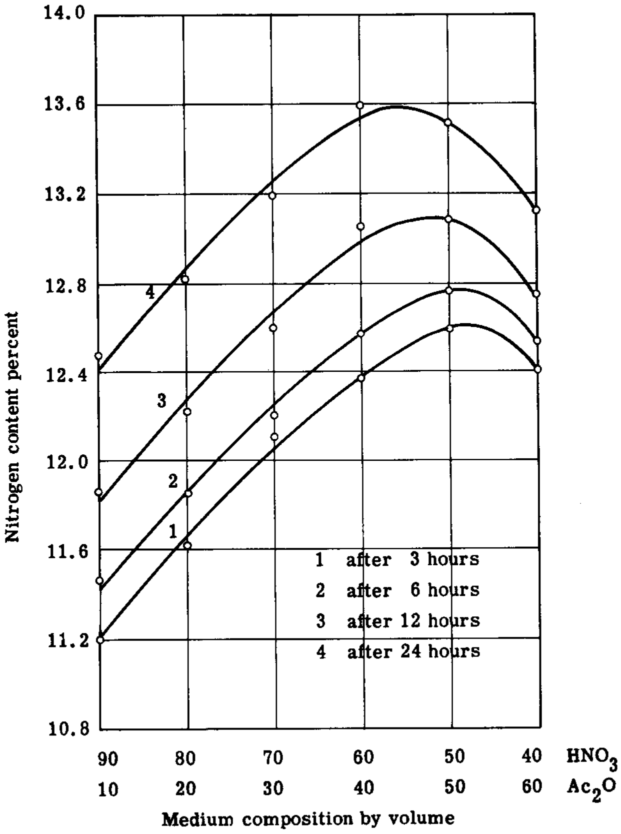


Figure 18

Table 16

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:50, Temperature 20°C

Medium composition by vol.	HNO$_3$	90	80	70	60	50	40
	Ac$_2$O	10	20	30	40	50	60
N content % After 3 hours		11.25	11.85	12.15	12.48	12.75	12.40
N content % After 6 hours		11.63	11.99	12.63	12.94	13.09	12.60
N content % After 12 hours		11.96	12.67	13.26	13.66	13.47	12.87
N content % After 24 hours		12.85	13.15	13.40	13.73	13.63	13.19

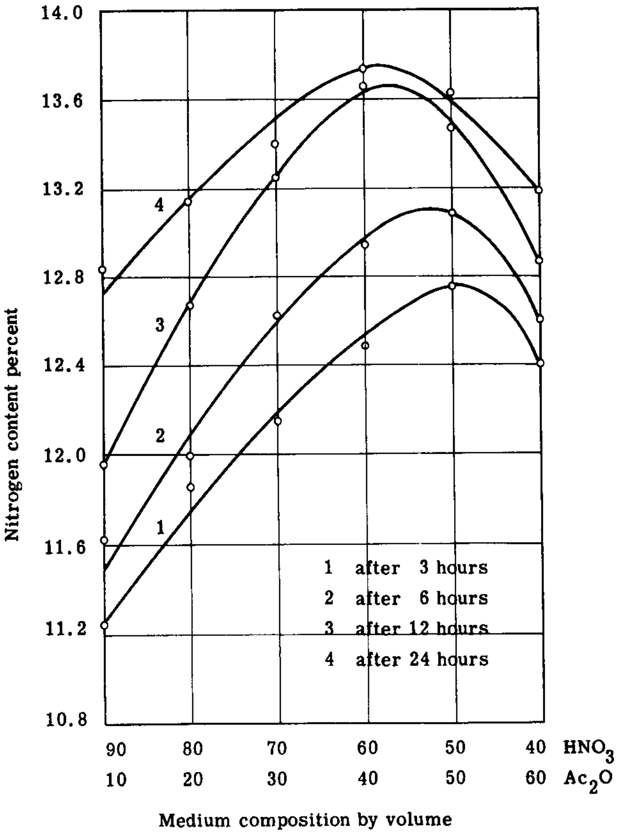


Figure 19

Table 17

Effect of reaction period and medium composition on the degree of nitration of amylose

Amylose-medium ratio = 1:50, Temperature 30°C

Medium composition by vol.	HNO_3	90	80	70	60	50	40
	Ac_2O	10	20	30	40	50	60
N content % After 3 hours		11.42	11.95	12.49	12.97	13.06	12.46
N content % After 6 hours		11.65	12.51	13.28	13.58	13.46	12.73
N content % After 12 hours		12.20	12.99	13.66	14.00	13.72	12.97
N content % After 24 hours		13.04	13.40	13.61	13.80	13.68	13.42

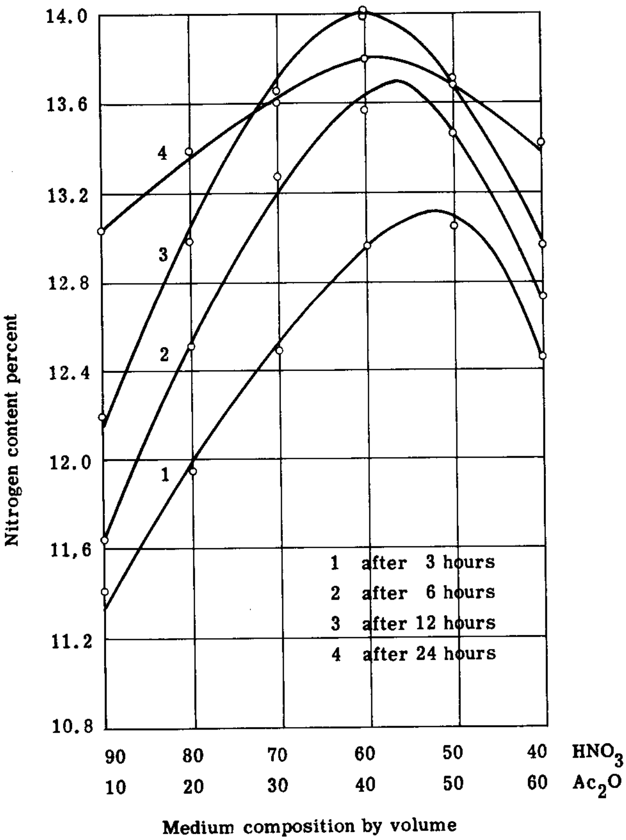


Figure 20

Effect of temperature and medium composition on the degree of nitration of amylose

amylose-medium ratio = 1:25, reaction period 3 hours

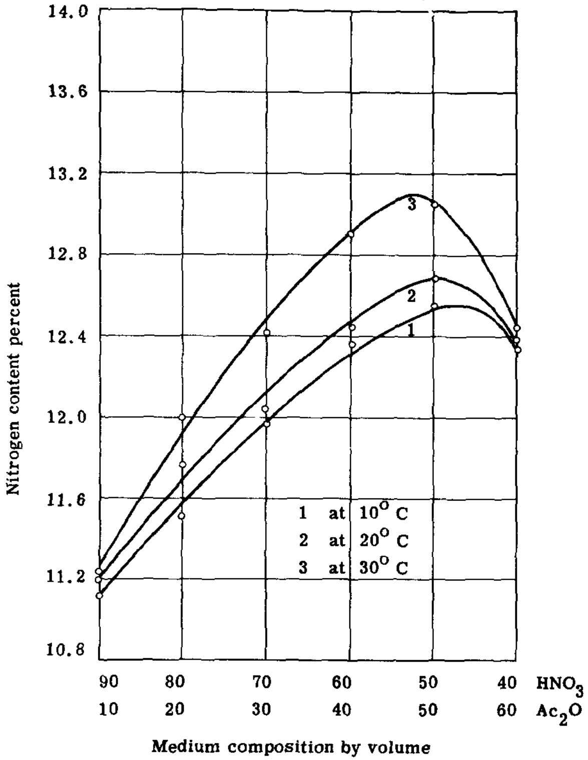


Figure 21

Effect of temperature and medium composition on the degree of nitration of amylose

amylose-medium ratio = 1:25, reaction period 6 hours

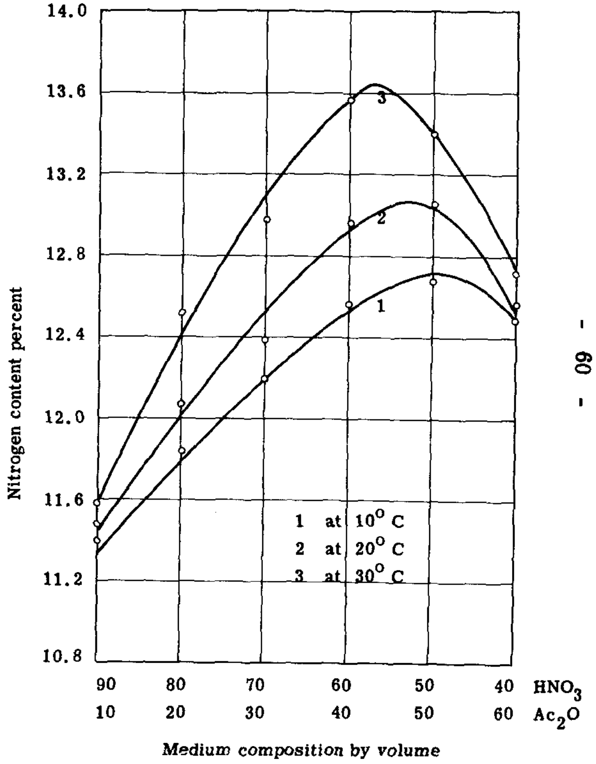


Figure 22

Effect of temperature and medium composition on the degree of nitration of amylose

amylose-medium ratio= 1:25, reaction period 12 hours

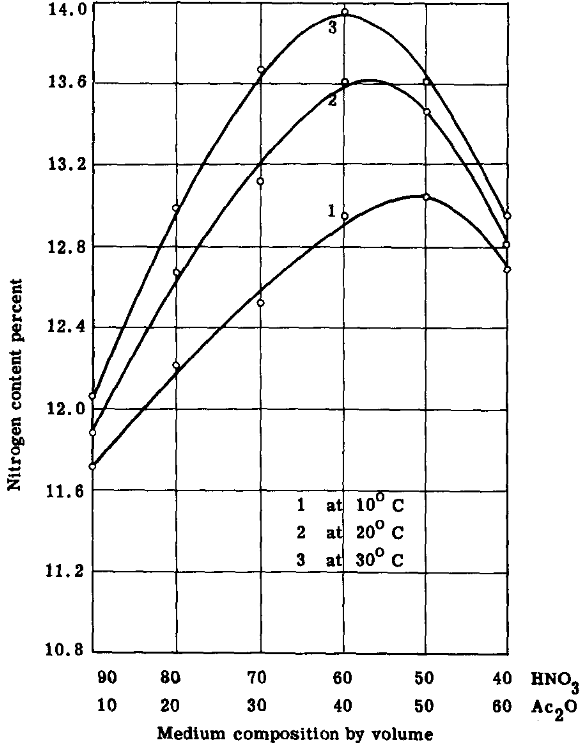


Figure 23

Effect of temperature and medium compisition on the degree of nitration of amylose

amylose-medium ratio = 1:25, reaction period 24 hours

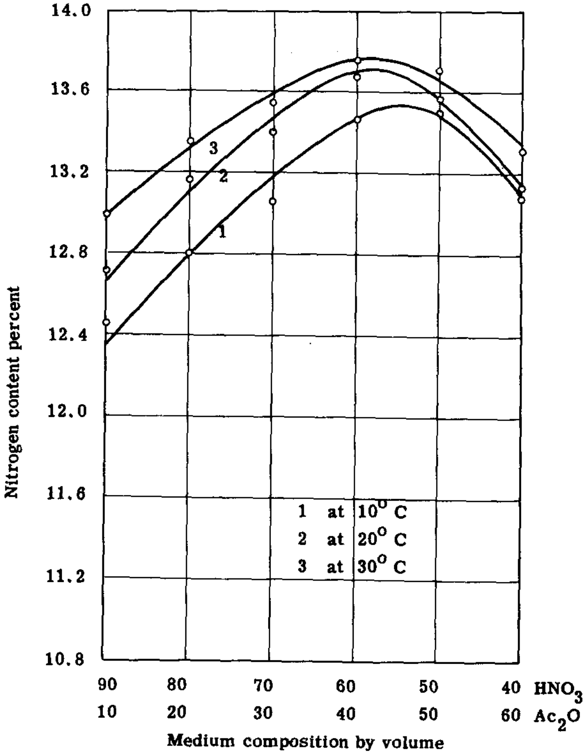


Figure 24

3.3 Nitration of amylopectin with nitric acid in the presence of pyridine

A point which cannot be overemphasized in any study of starch is the extreme susceptibility of this carbohydrate to degradation. Thus it is well to consider what treatment is harmful to starch and what treatment is not, a point always stressed by Meyer.

Of the various methods for preparing starch esters, only those involving pyridine as a catalyst find abundant support because the molecular weight of the starch is kept at a level approximating its original value. Attempts to glatinize starch directly in tertiary nitrogenous bases such as pyridine and quinoline have not been successful, since even boiling in such solvents is insufficient to burst the starch grains. If the starch grains are burst first, then it is possible to prepare colloidal solutions or pastes of the starch which are suitable for a homogenous single phase nitration. Pascu and Mullen II (59) found that it is possible to prepare colloidal solutions or pastes of starch in pyridine by boiling the starch in a pyridine-water mixture and then removing the water from the solution by azeotropic distillation.

3.3.1 Apparatus for the preparation of a paste of amylopectin in pyridine

The paste is prepared in an apparatus, illustrated in figure 25, consisting of a flask G having four ground joints. The central ground joint is equipped with a "Jena KPG well" D and a "Jena stirrer" E, the latter being driven by means of an electric motor A. To the second ground joint on a side of the flask is fitted a dropping funnel C. To the third ground joint on another side of the flask is fitted a double purpose condenser E, which functions either as a reflux condenser or as a Liebig condenser. In the latter case, a graduated cylindrical receiver I is fitted to it by means or a ground joint adapter. A thermometer B with its bulb reaching the bottom of the flask or facing the outlet of the double purpose condenser can be fitted to the fourth ground joint. The flask is heated by an electric oil bath H.

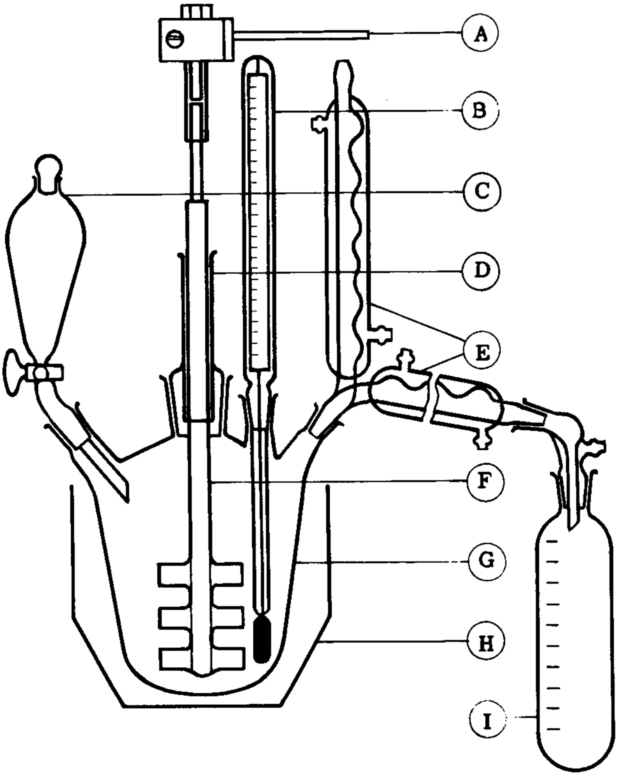


Figure 25 Apparatus for preparation of pyridine-starch pastes

3.3.2 Detailed procedure of the preparation of the paste

To a stirred mixture of 10 grams of amylopectin, previously dried at 100°C for two hours and 50 grams of dry pyridine is added dropwise 50 grams of deionized water. The mixture is heated under reflux at 100°C with stirring until a clear thin paste is obtained (about 20 minutes). To this paste 450 grams of dry pyridine are added, and after through mixing, the double purpose condenser is adjusted to the distillation position. The solvents are then distilled until the temperature of the vapours coming off have risen from an initial temperature of 92°C, which corrosponds to the boiling of the pyridine-water azeotrope, to 115°C, which corrosponds to the boiling temperature of pure pyridine. Removal of the water from the mixture is complete after distillation of 350 parts of the original 500 parts of pyridine. From the volume of the distillate, the composition of the paste can be calculated exactly.

3.3.3 Detailed procedure of the nitration of the paste

The nitration is conducted in the previously described nitrator illustrated in figure 11 with the slight modification that the end of the dropping funnel is above the surface of the liquid in the nitrator.

To attain an amylopectin-medium ratio 1:50, 220, 190, 160 or 130 ml. of nitric acid of specific gravity 1.5, according to the medium composition, are introduced into the flask. A rapid stream of cold tap water (6-8°C) is passed through the jacket, and appropriate volumes of dry pyridine to make 220 ml. with the volume of nitric acid present, are added from the dropping funnel accompanied by vigorous stirring. During the addition which requires about 10 minutes, the temperature is not allowed to raise above 40°C in order to prevent loss of the volatile pyridine nitrate. When all the pyridine have been added, the mixture is cooled 10 to 30°C below the operating temperatures and 66 grams of the paste having an amylopectin-pyridine ratio 1:10 are introduced into the funnel and allowed to drop slowly over the surface of the mixture accompanied by vigorous stirring. During the addition, which requires about 20 minutes, the temperature is not allowed to rise more than 5°C above the operating figure. When all the paste have been delivered, the funnel is washed with 20 ml. of cold nitric acid and the washing added to the mixture. The jacket is then connected to the circulating thermostat and the temperatur adjusted precisely to the operating figure. After replacing the dropping funnel by the sample-taking device, samples of about 75 ml. are withdrawn from the reaction mixture at intervals of 1, 2, 3, and 4 hours. Whenever a sample is withdrawn, it is immediately poured into one liter of ice-cold deionized water. The precipitated amylopectin nitrate is separated by filteration through a sintered glass funnel, washed with 100 ml. of 1% ammonia solution, and refiltered. It is then boiled in one liter of deionized water for one hour, filtered, and throughly dried at 40 to 45°C for three days.

To attain an amylopectin-medium ratio 1:100, the following changes are made:

(a) The added volumes of dry pyridine are such as to make 250 ml. with the volume of nitric acid added.

(b) 33 grams of the paste are used.

The different preparates of amylopectin nitrates are analyzed for nitrogen by the Bowman and Scott method.

3.3.4 Results of nitration

The results in tables 18 to 21 which are graphically shown in figures 26 to 29 show the effects of reaction period and medium composition on the degree of nitration of amylopectin when other parameters are kept constant according to the following classification:

Table	Figure	Amylopectin-medium ratio	Temperature
18	26	1 : 50	10
19	27	1 : 50	30
20	28	1 : 100	10
21	29	1 : 100	30

Figures 30, 31, 32, and 33 show the effect to temperature, amylopectin-medium ratio, and medium composition on the degree of nitration of amylopectin, after 1, 2, 3, and 4 hours respectively.

Table 18

Effect of reaction period and medium composition on the degree of nitration of amylopectin Amylopectin-medium ratio = 1:50, Temperature 10°C

Medium composition by vol.	HNO_3	80	70	60	50
	C_5H_5N	20	30	40	50
N content % After 1 hour		11.52	11.30	10.85	9.70
N content % After 2 hours		12.75	12.03	11.30	10.10
N content % After 3 hours		11.62	12.63	12.05	10.52
N content % After 4 hours		10.87	12.29	12.27	11.09

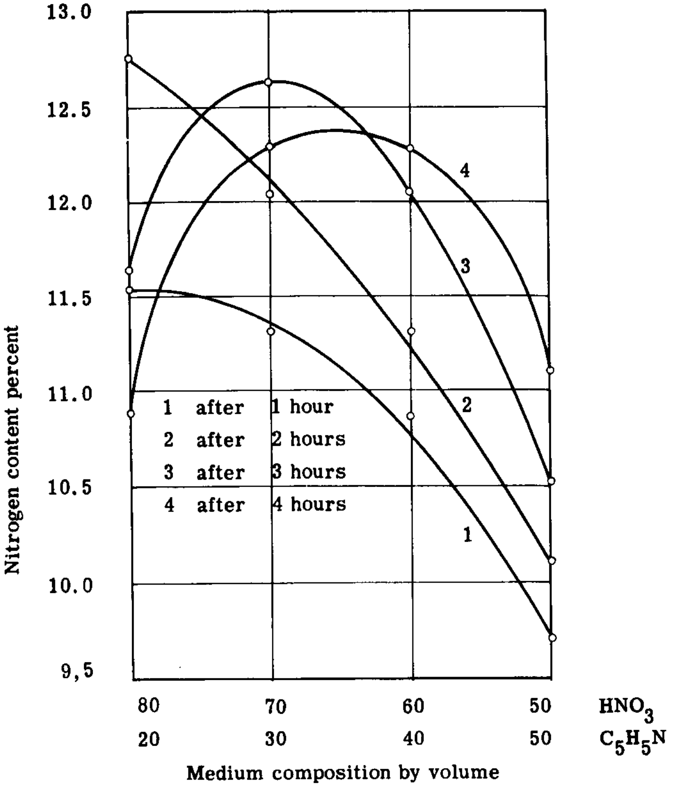


Figure 26

Table 19

Effect of reaction period and medium compostition on the degree of nitration of amylopectin

Amylopectin-medium ratio = 1:100, Temperature $10^{o}C$

Medium composition by vol.	HNO_3	80	70	60	50
	C_5H_5N	20	30	40	50
N content % After 1 hour		11.70	11.45	10.88	9.78
N content % After 2 hours		12.83	12.25	11.54	10.45
N content % After 3 hours		11.32	12.71	12.18	10.77
N content % After 4 hours		10.81	12.10	12.39	11.26

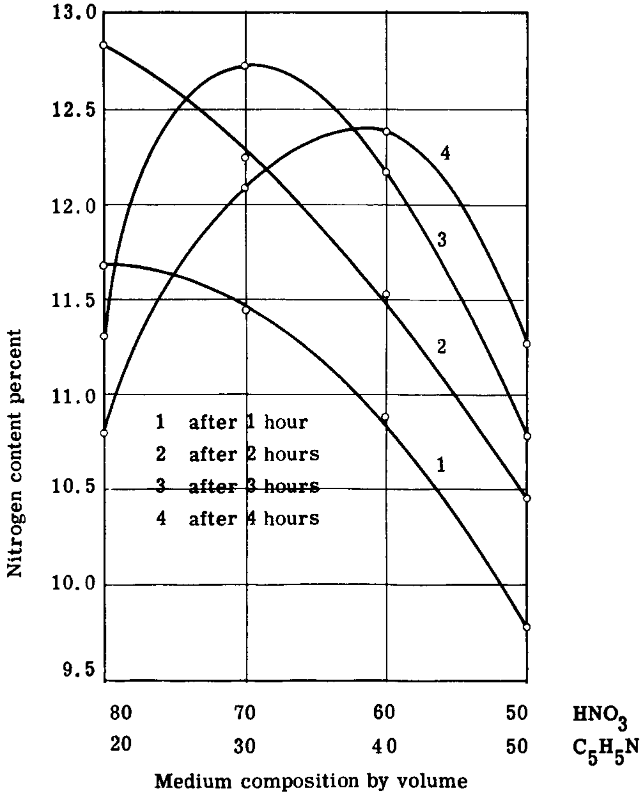


Figure 27

Table 20

Effect of reaction period and medium composition on the degree of nitration of amylopectin

Amylopectin-medium ratio = 1:50, Temperature 30°C

Medium composition by vol.	HNO_3	80	70	60	50
	C_5H_5N	20	30	40	50
N content % After 1 hour		11.92	11.57	10.88	9.93
N content % After 2 hours		12.79	12.50	11.61	10.76
N content % After 3 hours		11.25	12.75	12.28	11.00
N content % After 4 hours		11.50	12.00	12.48	11.40

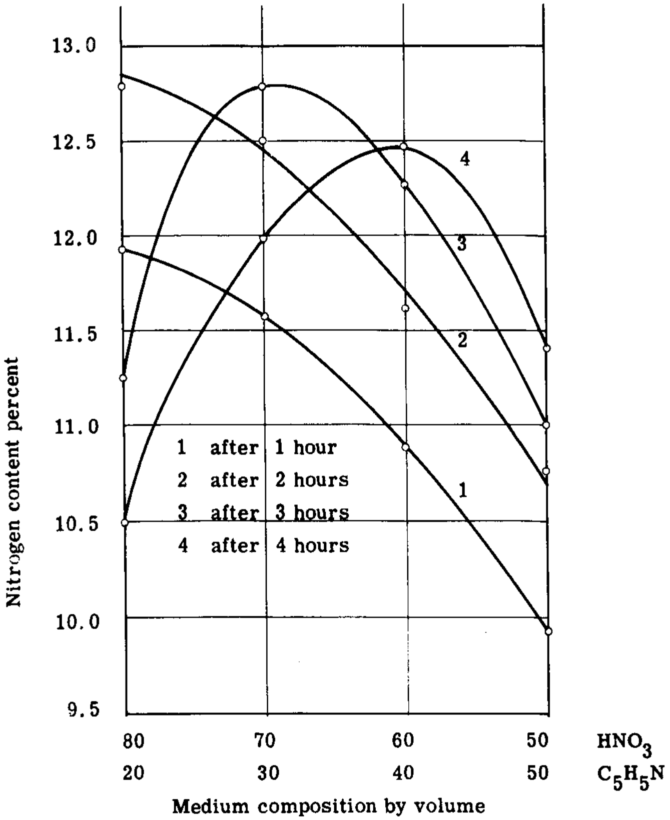


Figure 28

Table 21

Effect of reaction period and medium composition on the degree of nitration of amylopectin

Amylopectin-medium ratio = 1:100, Temperature 30°C

Medium composition by vol.	HNO_3	80	70	60	50
	C_5H_5N	20	30	40	50
N content % After 1 hour		12.21	11.66	11.07	9.97
N content % After 2 hours		12.71	12.45	11.68	10.87
N content % After 3 hours		10.49	12.18	12.35	11.18
N content % After 4 hours		10.36	11.81	12.55	11.15

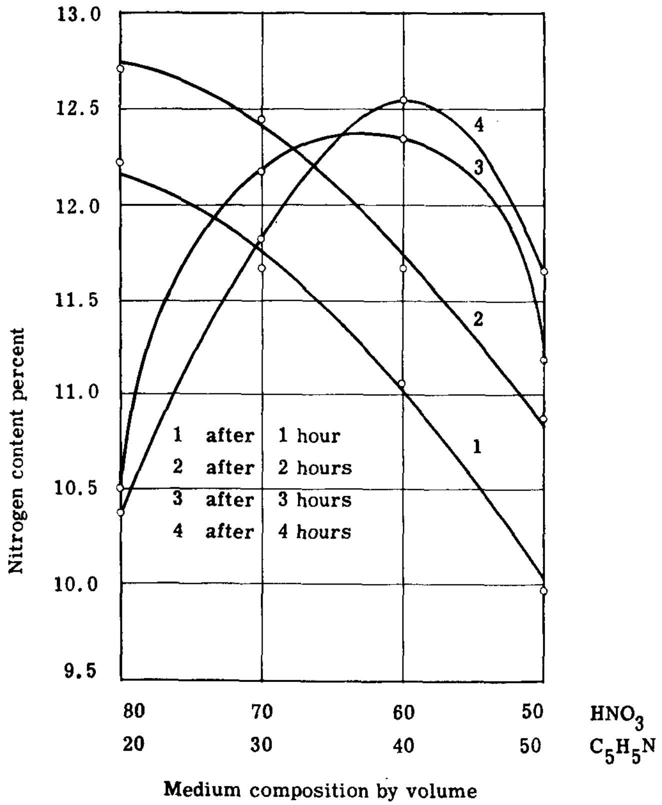


Figure 29

Effect of temperature, amylopectin-medium ratio, and medium composition on the degree of nitration of amylopectin

reaction period 1 hour

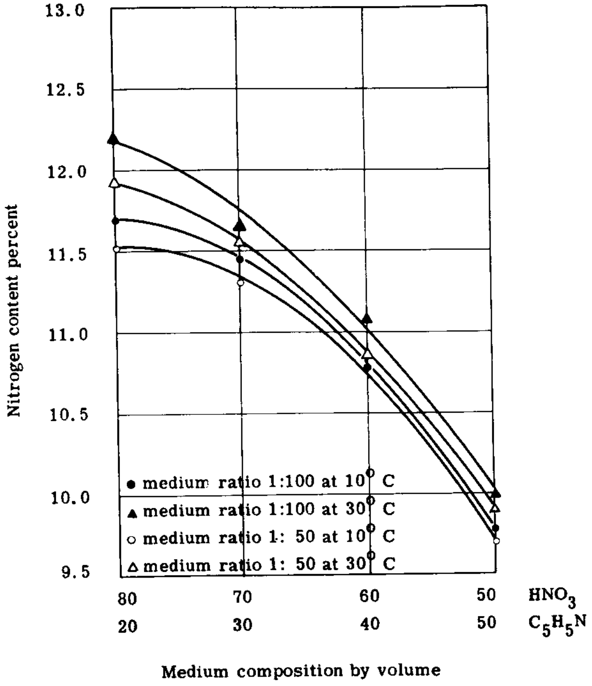


Figure 30

Effect of temperature, amylopectin-medium ratio, and medium composition on the degree of nitration of amylopectin

reaction period 2 hours

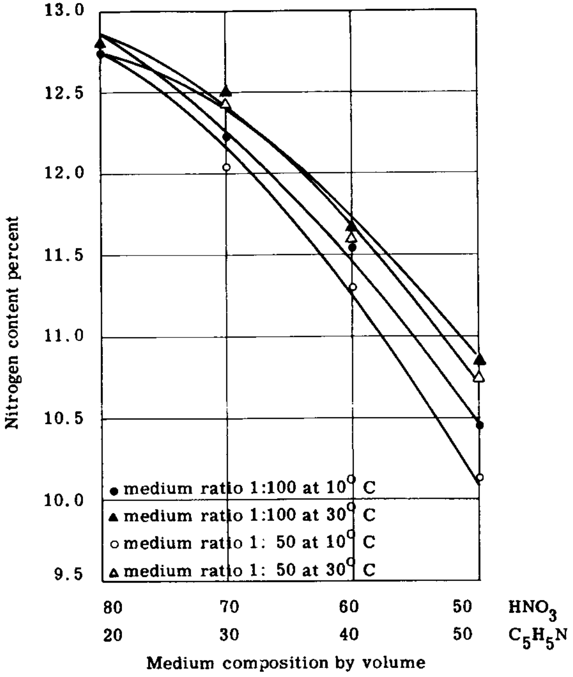
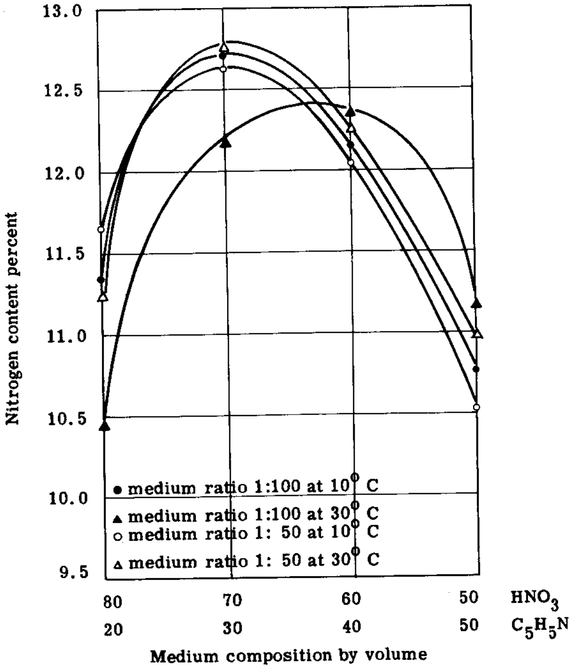


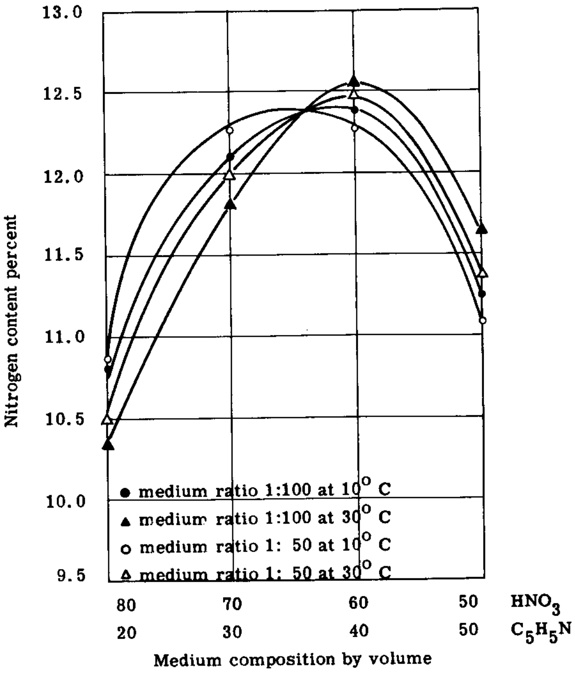
Figure 31



Effect of temperature, amylopectin-medium ratio, and medium composition on the degree of nitration of amylopectin

reaction period 3 hours

Figure 32



Effect of temperature, amylopectin-medium ratio, and medium composition on the degree of nitration of amylopectin

reaction period 4 hours

Figure 33

4. Discussion of nitration results

The nitration of starch is a smooth stoichiometric esterification reaction which is dependent on the nature of the nitrating medium. The degree of nitration is a function of the activity of the nitrating agent, and an important concept to insure effective nitration is the maintenance of high concentrations of the entities partaking in the reaction. In the present work, a study was undertaken to determine the effects on the degree of nitration of starch, of nitric acid-acetic anhydride mediums possessing relatively high nitrating activities, and of nitric acid-pyridine mediums possessing relatively weak nitrating power.

4.1 Nitric acid-acetic anhydride mediums

Orton (60) introduced the use of solutions of nitric acid in excess acetic anhydride as nitrating mediums, and Pictet, and Khotinsky (61) isolated acetyl nitrate from solutions of dinitrogen pentoxide in acetic anhydride. Also, various authors found the behaviour of Orton's mixture or acetyl nitrate to be similar to that of benzoyl nitrate, and very different from the group of reagents now recognized as reacting through the nitronium ion.

Gold, Hughes, and Ingold (62) studied the nitration by acyl nitrates, particularly benzoyl nitrate, and interpreted their results by their similarity with those of Cohen, and Wibaut (63) obtained by nitration with Orton's mixture. They showed that:

1. Added benzoic anhydride decreases the rate of nitration with benzoyl nitrate. This fact suggests that benzoyl nitrate may be exerting its property of nitration through a small stationary concentration of the persumably more effective entity, dinitrogen pentoxide, formed, along with benzoic anhydride, in the following rapidly reversible process:

$$2\ \mathrm{BzO.NO_2} \rightleftharpoons \mathrm{Bz_2O} + \mathrm{N_2O_5} \qquad (1)$$

2. Rates of nitration with benzoyl nitrate can be simulated, by employing mixtures of dinitrogen pentoxide and benzoic anhydride as the nitrating agents, provided that they contain some free benzoic acid.

3. The first order rate constants of the nitration of benzene in constant excess by mixtures of dinitrogen pentoxide, benzoic anhydride, and benzoic acid, increase with the concentration of dinitrogen pentoxide, when the concentrations

of benzoic anhydride and of benzoic acid are constant, and decrease with increasing concentration of either benzoic anhydride or benzoic acid when the other concentrations are fixed.

Gold, Hughes, and Ingold interpreted all these effects qualitatively by the hypothesis that benzoyl nitrate is exerting its nitrating power through the nitrating action of a small concentration of dinitrogen pentoxide, which is formed along with benzoic anhydride in the reversible reaction (1). It appears that this reaction attains equilibrium only slowly in the absence of acids, but that equilibrium is reached rapidly under the catalytic influence of benzoic acid. The latter is usually present in the systems considered, unless special measures are taken to exclude it.

However, this hypothesis does not explain the observed decrease of the rate of nitration in systems where the concentrations of benzoic acid are increased and the concentrations of dinitrogen pentoxide and benzoic anhydride remain fixed. In order to accommodate this finding, they assumed that in addition to the anhydride-anhydride equilibrium (1), an anhydride-acid equilibrium is set up, one form of which is shown in equation (2):

$$N_2O_5 + BzOH \rightleftharpoons BzNO_3 + HNO_3 \qquad (2)$$

Assuming equilibrium, it makes no difference whether they regard the benzoic acid as directly destroying dinitrogen pentoxide, as represented in equation (2), or as acting analogously on benzoyl nitrate, as in equation (3), thereby producing benzoic anhydride which then destroys dinitrogen pentoxide according to equation (1). Thus the alternative form (3) of the anhydride-acid equilibrium,

$$BzONO_3 + Bz.OH \rightleftharpoons Bz_2O + HNO_3 \qquad (3)$$

is not independent of (2). In other words, the equilibrium conditions for the reactions (1), (2), and (3) are expressible in terms of only two equilibrium constants. Reactions (2) and (3) evidently provide a mechanism for reaction (1), accommodating its acid catalysis. It follows that the presence of benzoic acid will always involve the presence of nitric acid; and that the catalysis of reaction (1), which is described as catalysis by benzoic acid, must not be regarded as specific to that acid. Such reactions should be subject to a general catalysis by acids. They concluded that, the case for assuming that benzoyl nitrate nitrates by the way of dinitrogen pentoxide seems as strong as qualitative evidence can make it.

According to the previous conclusions concerning the mode of nitration by benzoyl nitrate, Gold, Hughes and Ingold (62) expected nitration by acetyl nitrate, or by a solution of nitric acid in acetic anhydride, to proceed by way of dinitrogen pentoxide, formed in the following system of balanced reactions:

$$HNO_3 + Ac_2O \rightleftharpoons AcOH + AcNO_3$$

$$HNO_3 + AcNO_3 \rightleftharpoons AcOH + N_2O_5$$

and therefore, $$2\ AcNO_3 \rightleftharpoons Ac_2O + N_2O_5$$

Cohen and Wibaut's kinetic results for the nitration of benzene by solutions of nitric acid in an acetic anhydride solvent are, as they point out, very difficult to interpret, because of the simultaneous occurrance of the acetic anhydride. The recorded results indicate that the rate of nitration is increased by decreasing the concentration of acetic anhydride, a fact which they interpreted as a solvent effect. Gold, Hughes, and Ingold argued that if it were simply a solvent effect on nitration by nitric acid, or by some entity formed from nitric acid without the direct participation of acetic anhydride, then still greater rates should be obtained if the latter substance be omitted altogether. In testing this inference, they found that nitric acid does not nitrate benzene at $20^{o}C$ to any detectable extent. When a small quantity of acetic anhydride is added, however, nitration supervenes; whereas an excess of it again tends to suppress nitration.

The parallelism between these observations and those relating to the effect of added benzoic anhydride on the rate of nitration by benzoyl nitrate is evident. Gold, Hughes, and Ingold inferred, first, that the nitrating power of solutions of nitric acid in the presence of acetic anhydride is due to the formation of acetyl nitrate, and secondly, that the nitrate acts by a mechanism similar to that derived for nitration by benzoyl nitrate, i.e., by way of dinitrogen pentoxide, reversibly formed in the system of equilibria written above.

When amylose is nitrated by Orton's mixture, the following facts are established:

1. Orton's mixture shows optimum activity when the nitric acid is in slight excess of the stoichiometric ratio of acetyl nitrate formation. This falls in the region where the mixture contains equal volumes of nitric acid and acetic anhydride.

2. When the ratio of the components of Orton's mixture is changed, the degree of nitration of amylose decreases.

3. This optimum composition has a marked swelling effect on the amylose with a sudden evolution of heat, producing a mass whose viscosity is dependent on the amount of amylose present.

4. With increasing temperature, the degree of nitration is somewhat enhanced, being very marked in the region of optimum composition.

5. The degree of nitration increases with time till an equilibrium is reached, after which the nitrogen content of the product steadily decreases.

It now remains to interpret qualitatively these effects in the light of the preceeding discussion. As is noted before, there is a good deal of evidence that the nitrating properties of solutions of nitric acid in acetic anhydride are due to the formation of acetyl nitrate. The latter exerts its nitrating power through the nitrating action of a small concentration of dinitrogen pentoxide which is formed reversibly along with acetic anhydride:

$$2\,AcO.NO_2 \rightleftharpoons Ac_2O + N_2O_5 \qquad (4)$$

Most of the above effects can be interpreted by the hypothesis that the formation of dinitrogen pentoxide in the reversible reaction (4) is favoured in mediums originally containing equimolecular quantities of acetic anhydride and nitric acid, or a slight excess of the latter in the anhydride-acid equilibrium:

$$NHO_3 + Ac_2O \rightleftharpoons AcOH + AcO.NO_2$$

When the amount of acetic anhydride is incrased, dinitrogen pentoxide is destroyed in the equilibrium (4) with the consequent supress of the rate of nitration.

To explain the finding that the rate of nitration is decreased by increasing the concentration of nitric acid, it is assumed that the acetyl nitrate reacts with the excess nitric acid forming tetranitromethane according to the equation:

$$CH_3CO.ONO_2 + 3\,OH.NO_2 \longrightarrow C(NO_2)_4 + 3\,H_2O + CO_2$$

Consequently the equilibrium (4) is shilted to the left, decreasing the concentration of dinitrogen pentoxide and supressing the nitration rate.

The swelling phenomena of amylose in the above mentioned optimum composition cannot be overlooked. Swelling acts to loosen the intermicellar structure of amylose converting it to a state closely approximating a solution. In addition, there is an increase in volume due to the actual space required for the groups which are firmly attached to the starch chain and which promote swelling by either reducing the degree of hydrogen bonding or the area of contact between chains. This increase of volume will promote reactivity insofar as the presence of large solvating groups allows channels to be formed large enough to allow dinitrogen pentoxide to penetrate the amylose structure. Accordingly, the estrification equilibrium:

$$St.OH + N_2O_5 \rightleftharpoons St.O.NO_2 + HNO_3$$

will be shifted to the right in swelling mediums, accounting for higher degrees of nitration.

It is known that the reaction

$$St.OH + N_2O_5 \longrightarrow St.O.NO_2 + HNO_3$$

is slightly exothermic, i.e., accompanied by enthalpy decrease. It is reasonable to assume that the acid catalyzed equilibrium (4) is also catalyzed by increasing temperature, thus accounting for the observed increasing degree of nitration with temperature rise. However, this influence is limited to a temperature range up to 30°C or slightly higher. Since nitric acid is a good oxidizing agent, its oxidizing activity becomes more pronounced at higher temperatures.

When the esterification equilibrium is reached, the phenomena of denitration supervenes. Secondary reactions play a role in diluting the spent acid, thus favouring ester hydrolysis.

4.2 Nitric acid-pyridine mediums

The nitration of starch and its fractions in the presence of pyridine as a solvent furnishes a homogeneous single phase esterification reaction. When amylopectin is nitrated with nitric acid in the presence of pyridine, the following remarks are noted:

1. The acitivity of the medium is increased by increasing the quantity of nitric acid added.
2. The nitration is extremely fast and the esterification equilibrium is attained at a relatively low degree of nitration, followed by denitration.
3. The degree of nitration is favoured by increase of temperature and decrease of amylopectin concentration.

Hughes, Ingold, and Reed (64) studied the nature of nitric acid in various mediums, and found that in the presence of strong acids, nitric acid will be protonized to the nitric acidium ion. In the absence of any acid stronger than nitric acid, the latter will itself take the role of proton donor and the following equilibria will be set up:

$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$$

$$HNO_3 + H_2O \rightleftharpoons HNO_3,\ H_2O$$

From these equilibria it is clear that both the nitrate ion and water are anticatalysts towards nitronium ion formation.

In the presence of pyridine, nitric acid also acts as a proton donor according to the equation:

$$C_5H_5N: + HNO_3 \rightleftharpoons C_5H_5\overset{+}{N}H + NO_3^-$$

Thus in this medium, deprotonation of the nitric acidium ion is large, repressing the nitronium ion formation which is actually the active nitrating entity.

$$St.OH + NO_2^+ \rightleftharpoons St.O.NO_2 + H^+$$

Where the formation of the nitronium ion is very unlikely, it seems that either the nitric acidium ion or the molecular nitric acid is responsible for nitration.

$$St.OH + H_2NO_3^+ \rightleftharpoons St.O.NO_2 + H_2O^+$$

$$St.OH + HNO_3 \rightleftharpoons St.O.NO_2 + H_2O$$

In the light of these facts, it is clear that the activity of nitric acid in the presence of pyridine is greatly increased by increasing the quantity of nitric acid added.

An important concept to ensure effective nitration, is the maintenance of a high concentration of the effective nitrating agent. Eyring's equation of specific reaction rate signifies the fact that in covalent reactions, the free energy of formation of the intermediate reaction complex is large and the reaction rate is small. However, in polar solvents which favour ionic reactions, the free energy of formation of the intermediate reaction complex is small or negative and the reaction rate is large.

In mediums containing 70% nitric acid or more, the concentration of the effective nitrating entities is high enough to attain esterification equilibrium in two or three hours. Mediums containing less nitric acid are less active resulting in slower and less complete reaction. Naturally, when equilibrium is reached in ester formation the diluted spent acid furnishes a medium favouring hydrolysis, thus accounting for the phenomena of denitration.

Two additional factors bring about an increase in the degree of nitration, namely, increase in temperature and decrease in amylopectin concentration. It could be assumed that the equilibria furnishing the active nitrating entities are shifted by increasing temperature in directions favouring higher degrees of nitration. Naturally, increasing concentrations of the nitronium ion will favour higher degrees of nitration by maintaining the nitrating capacity of the medium near its maximum throughout the process. A higher percentage nitronium ions will penetrate the chain structure, increasing molecular collision and making every hydroxyl group accessible to esterification.

Part III

STABILIZATION OF STARCH NITRATES

A. THEORETICAL

1. Introduction

An elusive problem in the chemistry of explosives is that of stability. Nitrate esters, nitramines, and nitrocompounds which constitute the majority of explosive substances, show marked differences in stability. It can be said that nitrate esters are generally unstable, primary nitramines are less stable than secondary, and aliphatic nitrocompounds are most stable when they lack enolizable hydrogen.

Nitrates of starch, like the majority of nitric esters, are intrinsically unstable even at low temperatures. This liability to a slow exothermic spontaneous decomposition may accelerate to reach the order of an explosion. Instrinsic instability is attributed to the presence of traces of either free mineral acid or certain impurities which may be formed during the nitration process. The decomposition is accompanied with the liberation of oxides of nitrogen which cause a further catalytic action. Thus, a stabilization process consisting of boiling the nitrate ester in a large excess of water for variable periods of time is absolutely essential after nitration.

2. Review of literature

Escales (65) the well known German authority on explosives stated that "Nitrostarch has so far found but little practical application; the reason for this is to be found in the insufficient stability, in particular of the high nitrated products, ... ". Similarly, Marshall (66) stated that "In spite of the cheapness of the raw material, starch, it (nitrostarch) has never been able to displace nitrocotton; this is partly due to the instability of nitrostarch, ... ".

2.1 Stability properties

Mühlhauser (19) stated that all higher nitrates of starch are unstable and a stabilization treatment is necessary before they can be used as explosives. The instability is due to the union of some sulphonic acid groups in place of the nitrate groups with formation of the compound $C_{12}H_{14}O_4(ONO_2)_5OSO_3H$. He found that a mixture of nitrojute and nitrostarch in the proportion 3:1 containing 11.54% nitrogen, ignites at 160°C, and is stable up to 70°C.

Will and Lenze (20) reported that the nitrostarches prepared be either mixed acid and precipitated by water or nitric acid and precipitated by sulphuric acid, are comparatively stable at 50°C. They decompose with explosive violence at 194°C, and contain 14.04% and 13.90% nitrogen, respectively.

Sadtler (67) correlated the instability of nitrostarch to impurities originally present in starch, as well as to the complixity of the starch structure. By mixed acid nitration he was able to prepare starch nitrates containing 13.55, 13.14, and 13.00 per cent nitrogen. These products stand the Abel test at 79.4°C for 25, 30, and 32 minutes respectively.

Hackel and Urbanski (38) found that starch nitrates precipitated by water are more stable than those precipitated by sulphuric acid.

Berl and Kunze (43) nitrated starch by a nitric-phosphoric acid mixture to obtain a very stable product. When nitrating with mixed acids, a decrease in the water content decreases the stability of nitrostarch without increasing the nitrogen content, whereas the ignition point increases with an increase of water in mixed acid. With 6% water or more, the product does not deflagrate below 180°C. Treatment of the nitrated product with acetic acid has a higher stabilizing effect than with methyl alcohol, and the latter has a better stabilizing effect than water.

Young (68) reported that nitrostarch demolition explosive suffers appreciably in stability in comparison with TNT when stored for long periods. Acclerated tests indicate that nitrostarch is less stable than TNT although the former can be stored satisfactorily for some years.

2.2 Stabilization treatment

Several methods of stabilization treatment have been worked out. The presence of certain impurities in nitrostarch necessitates a purification treatment to reduce its liability to spontaneous decomposition. Nevertheless, purification treatment does not eliminate decomposition and liberation of oxides of nitrogen completely. Therefore, the idea of adding stabilizers to combine with the acidic decomposition products and thus prolong the life of nitrostarch, occured at an early date.

2.2.1 Stabilization by purification

Braunstein (69) patented a process for the stabilization of nitrostarch which deals with eliminating the last traces of free acid due to nitration as well as other impurities which are usually present. The process consists of treating the curde nitrostarch with a 10% solution of borax in the ratio of 5 to 1. After through agitation, the nitrostarch is allowed to settle, and the supernatent liquid drawn off. Finally, nitrostarch is washed with water to remove the borax and other impurities, and then dried in the customary manner.

Flurscheim (70) reported a procedure which involves boiling nitrostarch with several changes of fresh water until the acidity of the water is reduced to a minimum. The product is then boiled with water containing an amount of calcium carbonate sufficient to neutralize any remaining acid and is finally washed by boiling with a 2% solution of cyanamide or calcium cyanamide. After the final wash water, containing the stabilizer, is removed from the product by draining or by centrifuging; the product is dried in the usual manner. A small amount of the stabilizer will ordinarily be left in the dried product.

Anchor's (71) process of stabilization consists of boiling the washed nitrostarch repeatedly for twelve hours in a 0.5% solution of sulphuric acid. After this acid treatment, the product is suspended in water and a sodium soap added. The latter gives a mild basic reaction, tends to remove any fatty substances, and maintains a constant alkalinity of the solution. The solution is then agitated and heated to boiling. As the alkali liberated is used up, more of the salt dissociates thereby keeping the alkalinity of the water constant. The free fatty acid formed from the reaction between soap and acid unites with some of the soap molecules. This produces an insoluble compound which adheres to the particles of nitrostarch and accelerates their settling when agitation ceases. After the material is thus treated for four hours, it is boiled with water for four hours, followed by three additional treatments in fresh boiling water of three hours each. The excessive water is then removed in the hydro-extractor, and the moist starch died at 100°F. During the drying process the insoluble compound formed by the action of the free fatty acids on the soap molecules melts filling the pores and covering the grains of nitrostarch, and thereby producing a coating which prevents the absorption of moisture. This produces a stable nitrostarch which is as stable as the best nitrocellulose.

Snelling's (72) patent on the purification of nitrostarch is concerned with removal of unstable nitric acid esters contaminating it. The process involves the use of reducing agents which decompose all unstable nitric acid esters present. The nitrated starch is washed until the acidity is reduced to less than 1%. Twice the bulk of the wet nitrostarch of fresh water is added and an amount of sulpher dioxide amounting to 0.1 to 5% of the weight of nitrostarch is passed into the solution. The solution is then boiled by direct steam for one to two hours. A 2% solution of sodium thiosulphate acidified with sulphuric acid can also be utilized as a reducing medium at a temperature above 60°C. In fact, numerous other organic and inorganic reducing agents may be substituted for either of those already mentioned. Following the reduction, the nitrostarch is separated from the solution by filtration, and is further washed, neutralized, and dried.

Okada (34) has also investigated a method of stabilization of nitrostarch. The stabilization process consists of washing with hot alcohol which contains a little water or acetone.

Norton and Boyd (73) reported a method whereby nitrostarch is purified from residual acid and brought to an absolute neutrality, thus rendering it very stable. In accordance with this process, nitrostarch is washed with an alkaline solution of soluble tribasic phosphates and tetraborates, having a pH value between 12.0 and 8.3.

Nitrokémia Ipartelepek r.t. (74) patented a stabilization process which consists of the separation of nitrostarch from the nitrating acid mixture and treatment in an aquous solution with 50 to 90% ethyl alcohol followed by washing with alcohol and drying.

Stacho (75) treated nitrostarch with capillary-active aliphatic or aromatic organic compounds which contain polybasic mineral acid groups fixed on their carbon chains either directly or through N, O, or S atoms. The reaction medium must not dissolve or glatinize the nitrated starch.

Wyler and Boyd (76) discovered a combination of steps which will satisfactorily stabilize nitrostarch. After several washing steps to remove most of the free acid, the nitrostarch is stirred in a cold 1 to 3% solution of sodium bicarbonate for at least one hour. Then it is filtered and washed with water until the wash water has a pH of 7.1 to 8.2, and stirred again in a cold 0.1 to 0.2% solution of dicyandiamide for at least one hour at a temperature of 10 to 30°C. Then it is filtered and washed slightly with water so as to allow some dicyandiamide to remain in the filter cake. The filter cake is dried in a current of air at a temperature of 40 to 70°C.

Berl (74) found that treatment with swelling agents like alcohol or with mixtures of swelling and nonswelling agents like alcohol and benzene which are kept at or near the boiling point, is sufficient to remove unstable fractions from nitrated starch quickly. After repeated treatment with hot alcohol or hot alcohol-benzene mixtures, the material is dried by centrifuging.

Ashford, Cooke and Hibbert (78) applied fractional dissolution to nitrated starch accompanied by removal of ethanol soluble fractions. Hot and cold ethanol soluble fractions removed in this way contain 10 to 25% of the crude nitrate. The ethanol soluble fractions, consisting of low molecular weight and low nitrogen content material, are not stabilized by ethanol, whereas the insoluble portion is highly stabilized as a result of the ethanol treatment. Their results are given in table 22 and figure 34.

Table 22

Residual product	Moisture %	Nitrogen %	Abel test minutes	Brown fumes °C	Ignition point °C
After 7 hours of nitration	0.68	13.43	55	167	183
After 24 hours of nitration	0.55	13.96	30	173	185

The stabilization of starch nitrate by ethanol has been shown to be the result of a dual action, namely, (a) removal of highly unstable material of low molecular weight and nitrogen content, and (b) the conferring of increased stability by some unknown mechanism on the insoluble portion.

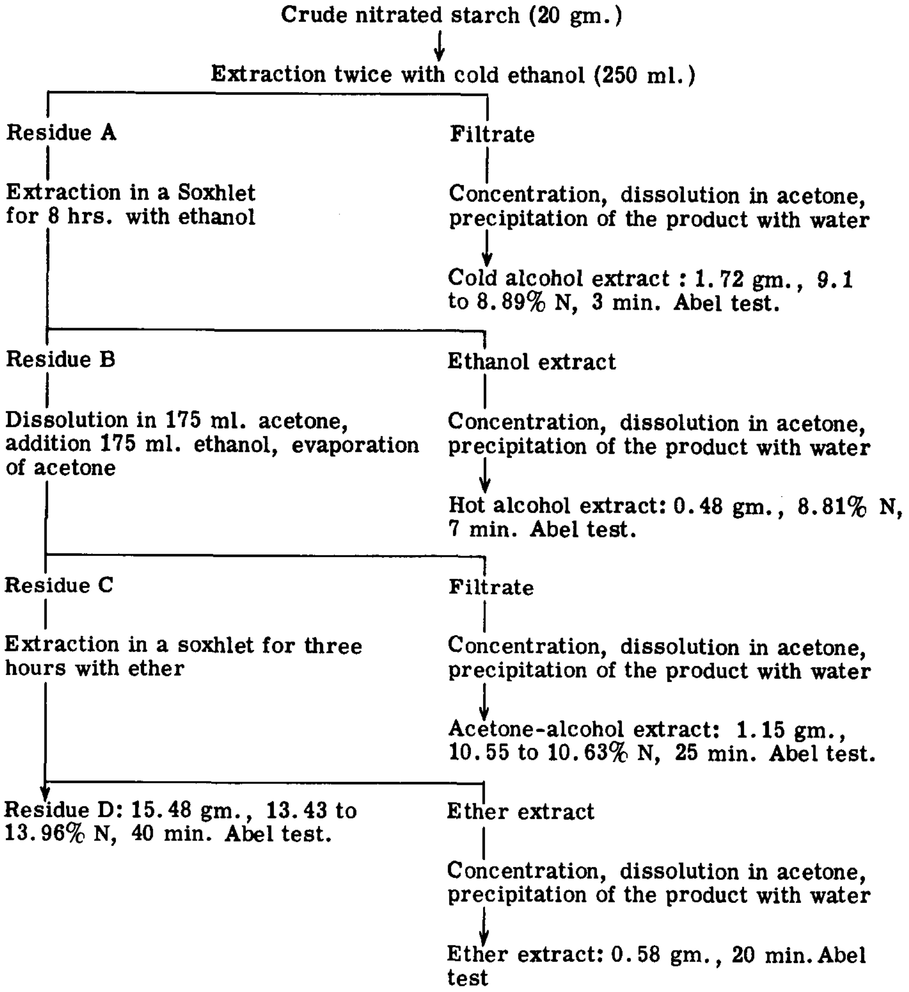


Figure 34

Fractional dissolution of whole starch nitrate

Ashford, Evans and Hibbert (79) fractionated corn starch into amylose and amylopectin by means of preferential adsorption on cellulose. These components are nitrated and the products fractionated by the previously mentioned methods and the relative stabilities and nitrogen contents of the nitrated fractions studied and are given in table 23. As justified by the Bergmann-Junk test, the unfractionated amylose nitrate has a greater stability than that from amylopectin. The solubility of the former in alcohol is only 20.5% whereas that of the latter is 86.7%. Alcohol treatment brings about an increase in the stability of the nitrates of both amylose and amylopectin in both the soluble as well as the insoluble fractions. The purified nitrates from amylose are more stable than those from amylopectin. The properties of the nitrates of the various fractions are in harmony with the branched chain structure of amylopectin and the linear strucutre of amylose.

Table 23

Product	Nitrogen %	Abel test min.	Bergmann-Junk test mgm. N
Amylose nitrate	12.96	10	7.28
Ethanol insoluble amylose nitrate	13.28	40	2.62
Ethanol soluble amylose nitrate	11.62	55	1.90
Amylopectin nitrate	12.25	4	15.20
Ethanol insoluble amylopectin nitrate	12.58	16	3.74
Ethanol soluble amylopectin nitrate	11.82	13	2.23

2.2.2 Stabilization by addition of stabilizers

Braunstein's (80) patents described three different nitrostarch compositions containing stabilizers. Nitrostarch can be mixed with 3 to 5% borax which renders the impurities harmless. A second composition which may be used consists of a 2 to 10% of lime mixture and a third consists of a mixture of 2 to 10% of sodium carbonate or bicarbonate.

Holmes (81) claimed usage of different inorganic and organic compounds to produce stable nitrostarch compositions, and his patents grouped the following stabilizers mostly in the proportion of 2 to 5 per cent: the orthophosphates, arsenate, chromate, carbonate, oxalate, palmetate, tartarate, polytartarate, and citrate of ammonia, oxamide, thiourea, nitroaniline, aniline oxalate, acetanilide, nitrotoluidine, toluidine oxalate, acettoluidine, and benzamide.

Nathan, Rintuol, and Baker (82) discovered that certain substances possess a very high degree of absorbtion for the harmful decomposition products, thus rendering nitrostarch more stable. These substances include derivatives of urea such as phenyl urea, methyl phenyl urea, and methyl diphenyl urea; ethers such as diphenyl ether, phenyl benzyl ether, ethyl naphthyl ether, and phenanthryl methyl ether; anilides including formanilid, acetorthotoluidid, acetparaanisidid, acetbetanaphthalid, benzorthoanisidid, phenylacetanilid, ethylacetbetanaphthalid, and phenylacetalphanaphthalid; and esters of substituted carbamic acids such as phenyl urethane, methyl phenyl urethane, and diphenylurethane. When added in the proportion of 5%, these classes of substances possess the property of combining or reacting with the decomposition products of nitric esters, thus preventing them from having an accelerating influence on the decomposition of these esters. The action of these substances when acting as stabilizers apparently consists partly in their becoming nitrated by the nitrogen peroxide and other injurious decomposition products, and partly in their reducing these acidic substances to compounds which have no action on nitric esters.

Snelling and Lams (83) stabilized nitrostarch by coating the particles with a thin film of heavy mineral oil. The coated particles are then treated with a mineral oil soluble organic stabilizing agent such as diphenylamine. The oil is used to prevent colloiding of the nitrostarch by the stabilizer because the stability of partly colloided nitrostarch is usually much less than that of the uncolloided form.

Snelling (84) stabilized nitrostarch ammonium nitrate explosives which undergo hydrolysis at elevated temperatures, leading to decomposition. The tendency to hydrolyze is overcomed by the addition of zinc or cadmium oxides or hydroxides in the proportion of 1 to 5%. Urea, dicyandiamid, trimethylamine, aniline, and ammonium or sodium borate in the proportion of 1% are suitable stabilizing agents.

Snelling and Wyler (85) discovered that pyridine exerts a marked and distinctive stabilizing effect upon nitrostarch. The effect is more marked when pyridine is used in conjunction with another neutralizing agent such as ammonia or monomethylamine.

B. EXPERIMENTAL

3. Determination of stability (86)

There are about forty different stability tests known. Nearly all of them are based on measurement of the decomposition products at somewhat elevated temperatures.

The stability tests can be conviently classified into three groups. The first group comprises those tests in which the explosive is heated at a temperature around 70°C, and the time required to produce a spot reaction is observed. The second group is that in which the sample is heated at a considerably higher temperature (up to 135°C), and the time required to produce a less sensitive spot reaction is observed. The third group comprises quantitative tests in which the sample is heated up to 135°C, and the oxides of nitrogen given off in a fixed period are measured. The Abel test belongs to the first group, while the Bergmann-Junk test belongs to the third group.

If nitrostarch is heated over 100°C at a rate of 5°C per minute, a point, called the ignition point, is reached a which explosion takes place. Although the ignition point is a measure of sensitivity to heat, it is sometimes carried out as a stability test. The reason for this is that impurities which cause instability have a marked effect in depressing the ignition point.

3.1 Determination of iginition point

3.1.1 Ignition point appratus (Julius Peters Model)

The apparatus shown in figure 35 consists of an electrically heated brass cylinder 5.0 cm. in hight, and 4.8 cm. in diameter. Four boreholes 4.4 cm. in depth, and 1.7 cm. in diameter are symmetrically made in the upper surface of the cylinder, their centers being 2.7 cm. apart. A precise thermometer shielded by a brass cylinder 10.0 cm. in height is screwed into the upper part of one hole. Test tubes 13.0 cm. in hight, 1.5 cm. in internal diameter, and 1.6 cm. in external diameter are placed in the other three holes. The heating is controlled by means of a sliding resistance.

3.1.2 Test method

Samples of 0.1 gram of nitrostarch dried at 45°C for three days are placed in each of the three test tubes. The brass cylinder is heated up to 100°C, and then the test tubes containing the samples are placed in their positions in the cylinder. The temperature is raised at a rate of 5°C every minute by means of the sliding resistance. The temperatures at which the three nitrostarch samples explode are noted. The mean of the three values is taken as the iginiton point.

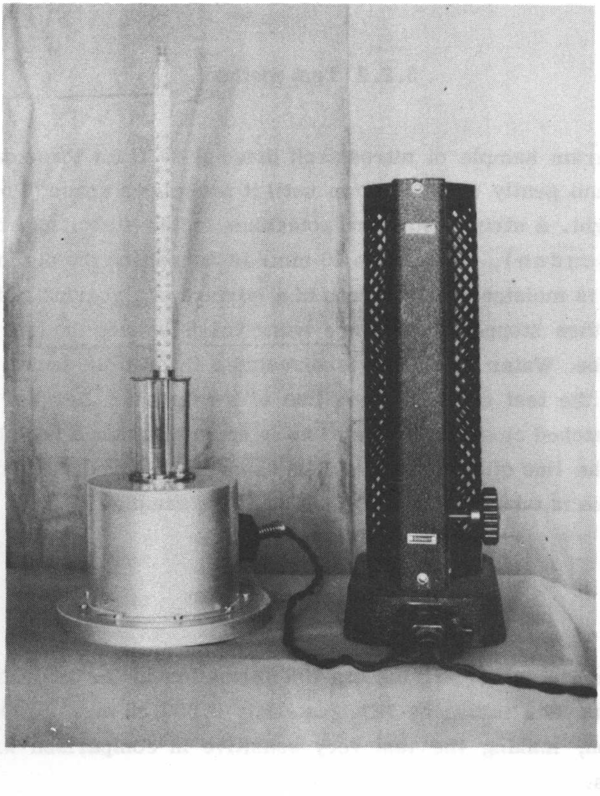


Figure 35 Ignition point apparatus (Julius Peters, Berlin)

3.2 Determination of stability by the Abel method

3.2.1 Modified apparatus

The apparatus consists of a glass tube C having precisely the dimentions shown in figure 36. The tube is stoppered by a ground stopper A having an extending rod inside the tube to which a platinum hook B is sealed. The lower part of the tube is double walled to a length of 7.5 cm., so as to allow for precise regulation of temperature at 65.5°C by passing water through the jacket D by means of a forced circulation thermostat.

3.2.2 Test method

A 1.3 gram sample of nitrostarch dried at 45°C for three days in placed in the tube and gently pressed down until it occupies a space of not more than 30 mm. in hight. A strip of standard potassium iodide-starch paper (Johnson & Sons, London), 20 mm. by 10 mm. is hanged on the platinum hook and its lower half is moistened with a drop of a mixture of glycerine and water (1:1). The tube is then stoppered and care being taken to hang the test paper freely inside the tube. Water at 65.5°C is circulated through the jacket and the time is noted. As the test continues, the line of demarcation between the wet and dry halfs is watched closely. The test time is complete when a faint brown colour appears on the line of demarcation. The experiment is repeated five times and the mean value is taken as the Abel value of the sample

3.2.3 Test principle

The mechanism underlying the tint formation is the liberation of iodine from the potassium iodide by NO_2 gas. Only 0.000135 mg. of NO_2 gas effects tint formation, making the test very sensitive in comparison with all other stability tests.

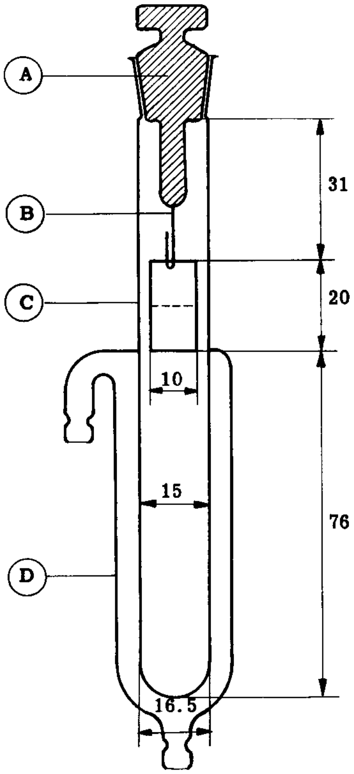


Figure 36 Modified Abel heat test apparatus

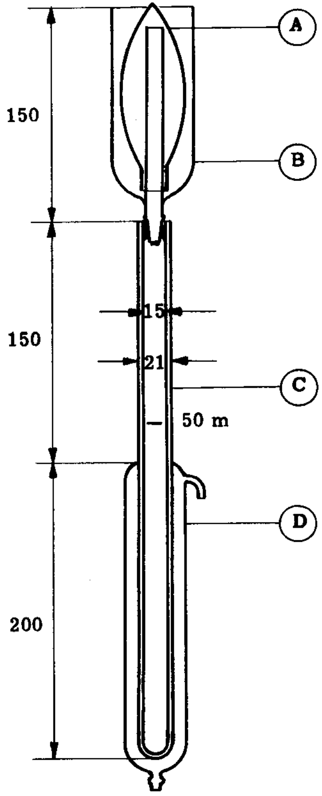


Figure 37 Modified Bergmann-Junk apparatus

3.3 Determination of stability by the Bergmann-Junk method

3.3.1 Modified Apparatus

The apparatus consists of a thick walled glass tube C having precisely the dimentions shown in figure 37. The tube is stoppered by a ground joint carrying an absorption device, which consists of a beaker B through which a tube is sealed centrally to connect the ground joint. A bulb A is inverted over the central tube in the beaker. The lower part of the tube is double walled to a length of 20 cm., so as to allow for the precise regulation of temperature at 132°C by passing Dowtherm through the jacket D by means of a forced circulation thermostat. On the wall of the tube, a mark is made corrosponding to 50 cc.

3.3.2 Test method

One gram (two grams in the standard test) of nitrostarch dried at 45°C for three days is placed in the tube. The ground glass stopper is slightly greased and inserted in the ground joint of the tube. The beaker of the absorption device is half-filled with water and the central tube is covered with the bulb. Dowtherm at 132°C is circulated through the jacket and the heating is continued for two hours. Then the heating is stopped and the jacket freed from the liquid. As the air in the tube contracts, the water is drawn inside the tube from the beaker through the central tube. The absorption device is washed out into the tube and the volume is brought up to the 50 cc. mark. The liquid is then filtered, 25 cc. of the filterate oxidized by 1 cc. 0.5 normal $KMnO_4$, and the nitrogen then estimated by the Schultze-Tiemann method (87). The experiment is repeated five times and the mean value expressed as mgm. nitrogen per gram nitrostarch is taken as the Bergmann-Junk value of the sample.

3.4 Tolerances in the results of stability tests

Tolerances existing in the results of stability tests are mainly due to the high instability of amylose and amylopectin nitrates before the stabilization treatment. The limits of tolerance are found to cover a range of ± 11% before stabilization and ± 2% after four hours of boiling. The Bergmann - Junk test values marked (*) are found by interruption of the heating at the proper time and correction of the test value by direct proportionality, as the material is too unstable to withstand the test

4. Stabilization of starch nitrates

The newly studied method of nitration of starch components necessitated a study of the conventional purification treatment which includes boiling with water for various lengths of time.

4.1 Stabilization by boiling with water

Samples of 20 grams of starch, amylose, and amylopectin are each nitrated at 10°C in a mixture containing equal volumes of fuming nitric acid and acetic anhydride. One gram of the carbohydrate is added to every 15 cc. of the nitrating acid and after 15 hours the reaction mixture is poured into an excess of ice cold deionized water. The precipitated nitrate is collected on a sintered glass funnel and washed with boiling water untill the filterate is neutral. A first sample is taken and the remaining precipitate boiled in two liters of deionized water for one hour. The nitrate is then filtered, washed with boiling water untill the filterate is neutral, and a second sample taken. The treatment is similarly repeated for the third, fourth, and fifth samples. The five samples after thorough filteration are dried at 40 to 45°C for three days.

The different preparates are then analyzed for nitrogen, ignition point, and stability.

The results in table 24 which are graphically shown in figures 38 to 41 show the effect of boiling with water on the nitrogen content, ignition point, and stability of starch, amylose, and amylopectin nitrates.

4.2 Stabilization by boiling with water following neutralization with ammonia

The same procedure as that described above is followed, except that the precipitate is washed with one liter of 1% ammonia just before each boiling treatment.

The results in table 25 which are graphically shown in figures 42 to 45 show the effect of boiling with water, following neutralization with ammonia, on the nitrogen content, ignition point, and stability of starch, amylose, and amylopectin nitrates.

4.3 Stabilization by fractionation with alcohol

Starch, amylose, and amylopectin nitrates are prepared and stabilized by boiling with water for four hours without washing with ammonia. Ethanolic extraction is carried out according to the method recommended by Ashford, et al. (78, 79).

4.3.1 Fractionation of starch nitrate

Eighty grams of nitrated starch dried at 40 to 45°C for three days are suspended in one liter of absolute ethanol and vigorously stirred at 40°C for three hours. The undissolved residue is separated by filteration, and the ethanolic extract concentrated to a small volume at 50°C under 20 to 25 mm., until the dissolved nitrate is precipitated. After precipitation is completed by the addition of petroleum ether, the nitrate is separated by filteration and dried at 50°C. The product is then heated under reflux with deionized water for 24 hours to ensure the complete removal of ethanol. The insoluble residue is treated in a similar manner.

The results in table 26 show the effect of fractionation of the starch nitrate with ethanol on the nitrogen content, ignition point, and stability of the fractions.

4.3.2 Fractionation of amylose and amylopectin nitrates

Eighty grams of each nitrate dried at 40 to 45°C for three days are placed in 1500 cc. of absolute ethanol and vigorously stirred at 40°C for ten hours. The residues are separated by centrifuging and filteration, and the ethanolic extract in each case evaporated to a small volume at 30 to 35°C under 20 to 25 mm. In the case of the amylopectin, the extract is precipitated by the addition of petroleum ether of boiling point 30 to 50°C. In the case of the amylose, the extract is precipitated by the addition of water. The extracted nitrates are then collected by filteration and boiled with deionized water under reflux for 24 hours to ensure the complete removal of ethanol. The insoluble residues are treated in a similar manner.

The results in table 26 show the effect of fractionation of the amylose and amylopectin nitrates with ethanol on the nitrogen content, the ignition point, and the stability of the fractions.

Table 24

Stabilization of starch, amylose & amylopectin nitrates
Effect of boiling with water (acidic medium)

Stabilization treatment		N content %	Ig. pt. °C	Abel test min.	B.-J. test mgm. N/gm.
Starch nitrate	Before stabilization	13.93	145.5	1	40.91*
	After 1 hr. boiling	13.71	150	2	25.75*
	After 2 hrs. boiling	13.50	158	4	15.30
	After 3 hrs. boiling	13.39	169	8	8.01
	After 4 hrs. boiling	13.35	177	12	5.55
Amylose nitrate	Before stabilization	13.99	149	1	38.33*
	After 1 hr. boiling	13.76	156	3	19.99
	After 2 hrs. boiling	13.55	160.5	6	10.10
	After 3 hrs. boiling	13.46	173	10	7.11
	After 4 hrs. boiling	13.39	179	16	3.88
Amylopectin nitrate	Before stabilization	13.89	144	1	41.92*
	After 1 hr. boiling	13.69	147.5	2	26.00*
	After 2 hrs. boiling	13.48	155	2	25.88*
	After 3 hrs. boiling	13.37	162.5	4	15.34
	After 4 hrs. boiling	13.32	176	7	9.21

Effect of boiling in acidic medium on the nitrogen content of amylose I, starch II, and amylopectin III nitrates

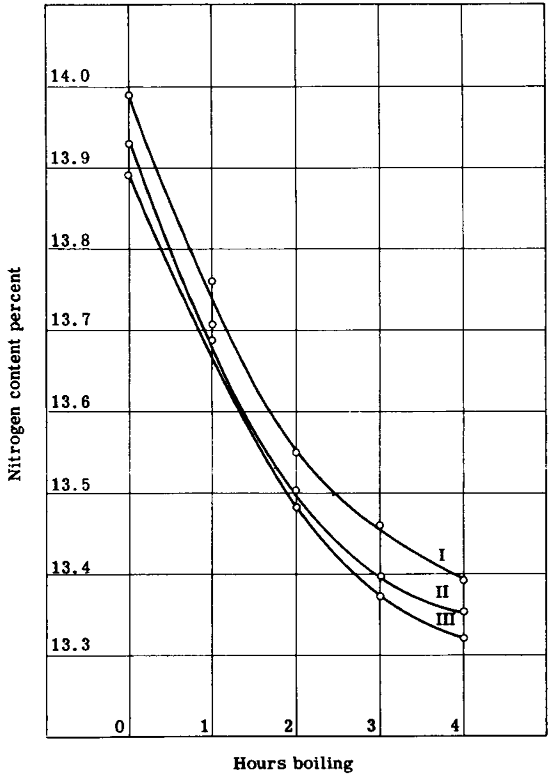


Figure 38

Effect of boiling in acidic medium on the ignition point of amylose I, starch II, and amylopectin III nitrates

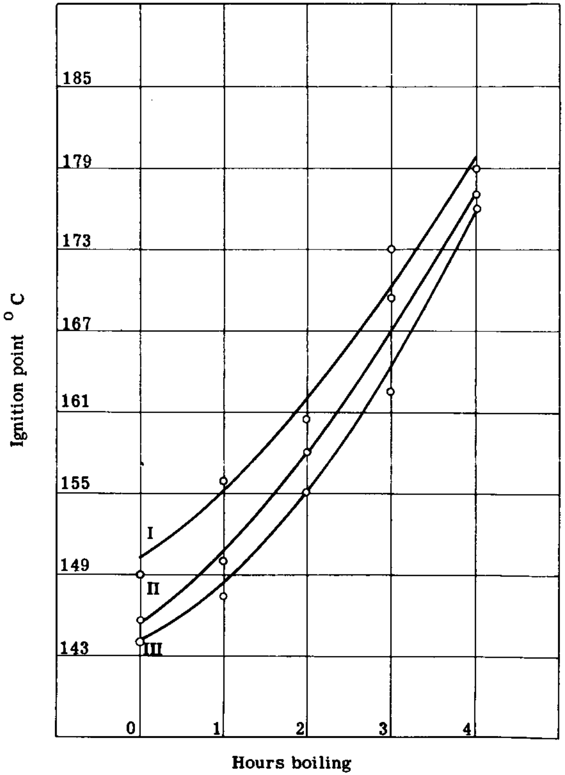


Figure 39

Effect of boiling in acidic medium on the Abel values of amylose I, starch II, and amylopectin III nitrates

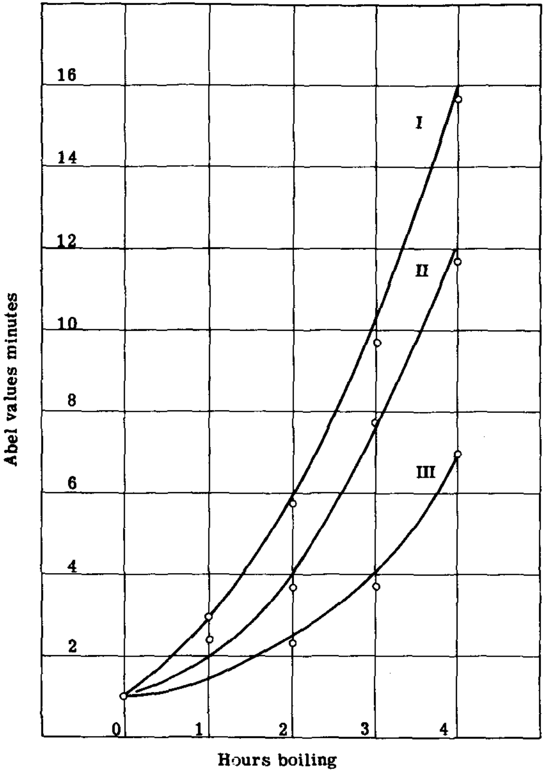


Figure 40

Effect of boiling in acidic medium on the B.-J. values of amylose I, starch II. and amylopectin III nitrates

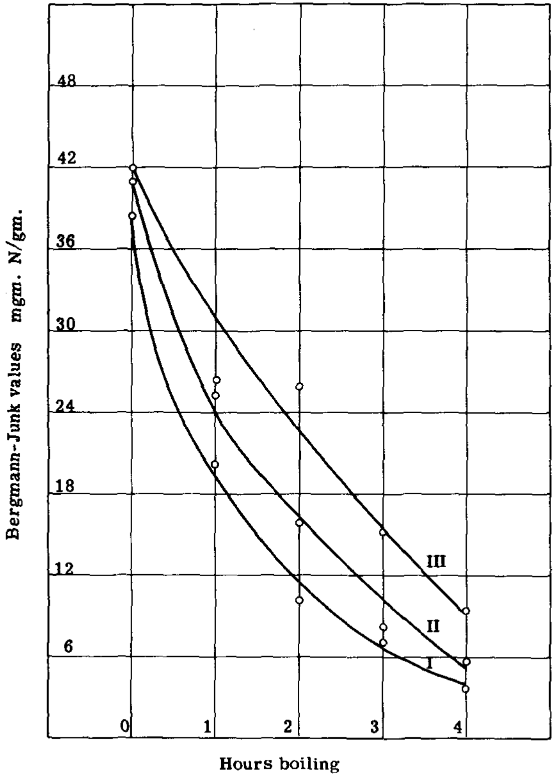


Figure 41

Table 25

Stabilization of starch, amylose & amylopectin nitrates
Effect of boiling with water following washing with ammonia (alkaline medium)

	Stabilization treatment	N content %	Ig. pt. °C	Abel test min.	B.-J. test mgm. N/gm.
Starch nitrate	Before stabilization	13.93	145.5	1	40.91*
	After 1 hr. boiling	13.64	151.5	2.5	23.90*
	After 2 hrs. boiling	13.47	159.5	4.5	14.44
	After 3 hrs. boiling	13.37	170.0	8	9.62
	After 4 hrs. boiling	13.32	183.5	14	4.75
Amylose nitrate	Before stabilization	13.99	149	1	38.33*
	After 1 hr. boiling	13.73	155.5	3	15.30
	After 2 hrs. boiling	13.52	167.0	6	9.90
	After 3 hrs. boiling	13.43	173.0	11	4.81
	After 4 hrs. boiling	13.37	188.0	17	3.00
Amylopectin nitrate	Before stabilization	13.89	144	1	41.92*
	After 1 hr. boiling	13.54	150.5	1.5	28.00*
	After 2 hrs. boiling	13.37	156.0	3.5	22.00*
	After 3 hrs. boiling	13.27	167.0	5	13.45
	After 4 hrs. boiling	13.25	179.0	8	8.11

Effect of boiling in alkaline medium on the nitrogen content of amylose I, starch II, and amylopectin III nitrates

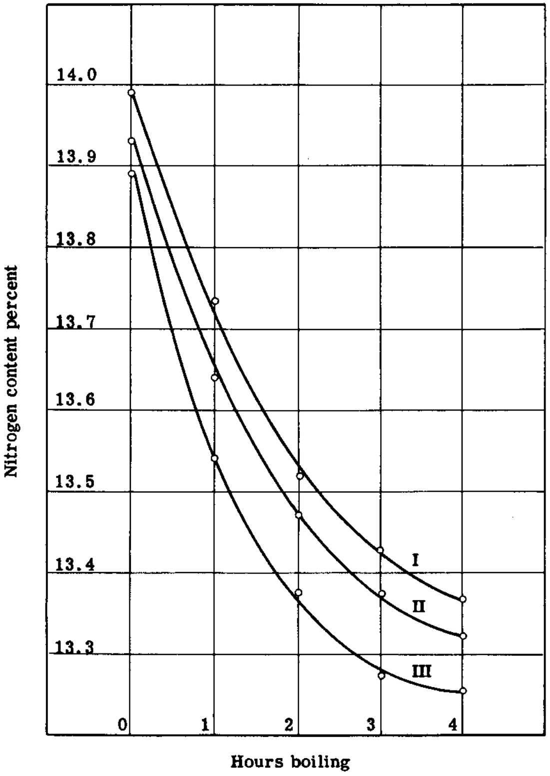


Figure 42

Effect of boiling in alkaline medium on the ignition point of amylose I, starch II, and amylopectin III nitrates

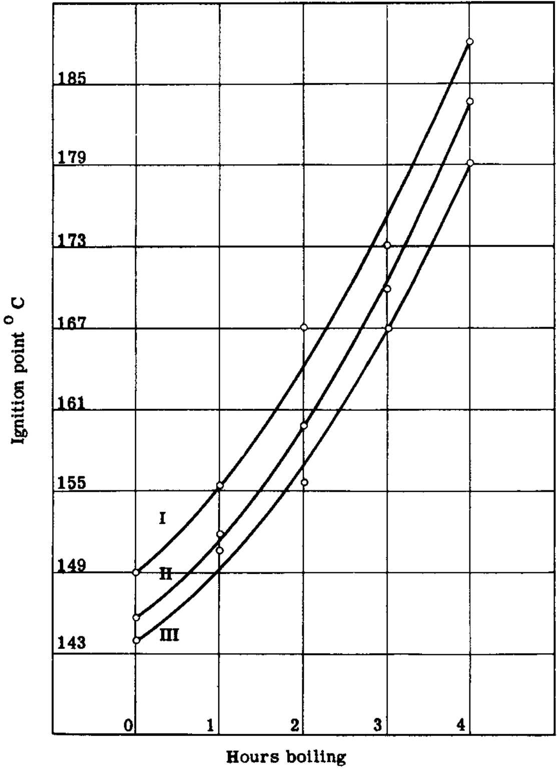


Figure 43

Effect of boiling in alkaline medium on the Abel values of amylose I, starch II, and amylopectin III nitrates

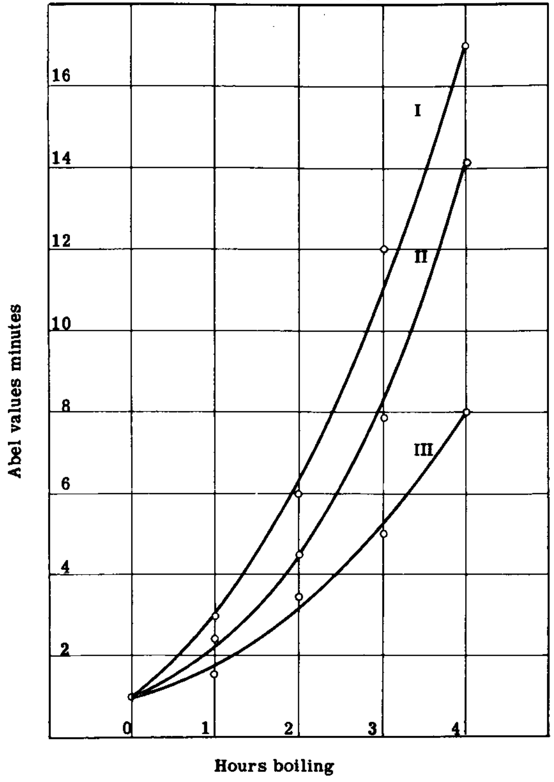


Figure 44

Effect of boiling in alkaline medium on the B.-J. values of amylose I, starch II, and amylopectin III nitrates

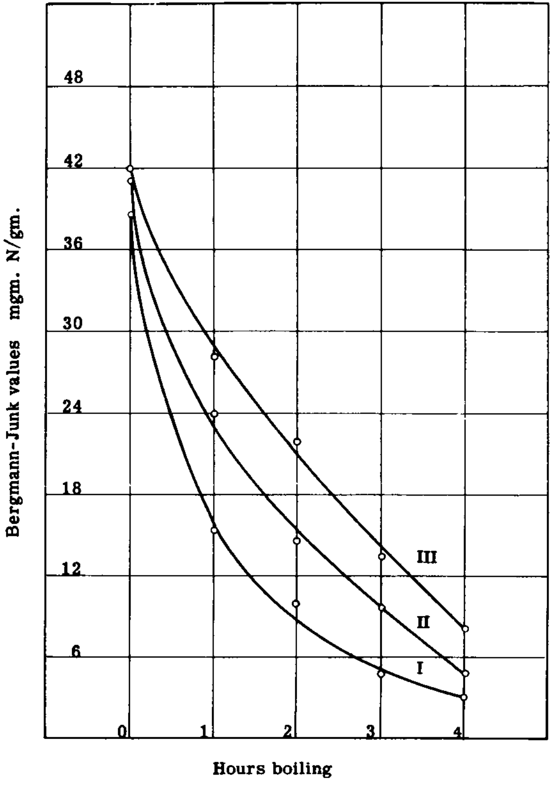


Figure 45

Table 26

Stabilization of starch, amylose & amylopectin nitrates
Effect of fractionation with ethanol

Fractions	N content %	Ig. pt. °C	Abel test min.	B.-J. test mgm.N/gm.
Total starch nitrate	13.35	177	12	5.55
Ethanol soluble starch nitrate	13.10	177	28	2.72
Ethanol insoluble starch nitrate	13.60	180	33	2.61
Amylose nitrate	13.39	179	16	3.88
Ethanol sol. amylose nitrate	13.11	180	41	2.35
Ethanol insol. amylose nitrate	13.59	184.5	49	2.22
Amylopectin nitrate	13.32	176	7	9.21
Ethanol sol. amylopectin nitrate	13.08	177	18	3.01
Ethanol insol. amylopectin nitrate	13.59	178	21	2.92

5. Discussion of stabilization results

It was already pointed out that instability in the nitrates of starch or its fractions is mainly due to the presence of small amounts of free mineral acid, combined sulphuric acid, or certain nitrated oxidation products. In a nitrating medium composed of nitric acid and acetic anhydride, tetranitromethane is produced to a slight extent and contaminates the nitrated product. This compound acts as a powerful oxidizing agent owing to the large excess of oxygen that it contains and when in contact with water it undergoes some hydrolysis even at ordinary temperature. It is thermally very stable in the pure state, but in the presence of even atmospheric moisture it produces a blue coloration on a potassium iodide-starch paper in less than one minute. Indicating the rapid formation of acid.

The following facts can be noted about nitrated starch or its fractions after being stabilized by boiling with water:

1. Repeated boiling with water in either an acidic or an alkaline medium causes a decrease in the nitrogen content.
2. Repeated boiling with water in either an acidic or an alkaline medium causes a gradual increase in the stability as judged by increasing ignition points, increasing Abel periods, and decreasing Bergmann-Junk values.
3. Higher denitration and higher stability are rather attained in alkaline than acidic mediums.
4. Amylose nitrate is more stable than whole starch nitrate, and amylopectin nitrate is the least stable.
5. Stability is greatly improved after a short period of boiling in case of nitric acid-acetic anhydride nitration compared with mixed acid nitration.

It now remains to interpret the effects of boiling nitrated starch or its fractions with the general causes of instability and the behaviour of tetranitromethane. A decrease in nitrogen content is caused by the hydrolysis of the nitrate esters and the consequent liberation of nitric acid. A further decrease in nitrogen content is due to the elimination of tetranitromethane which is volatile with steam and contains double as much nitrogen as contained in starch nitrates. The effect of boiling is to wash out any free mineral acid and thus nullify its detrimental effect and volatilize the highly unstable tetranitromethane. These two effects are reflected in the improvement of stability as judged by increasing ignition points, increasing Abel periods, and decreasing Bergmann-Junk values. A point which should be emphasized is that the ignition point can be increased up to 188°C, and the Bergmann-Junk value decreased to 3.00 mgm. nitrogen by this procedure, values which are of the same order as those of nitrocellulose specifications. On the other hand, the Abel period is only increased to 17 minutes, a value far beneath the nitrocellulose specifications for this test. This is due to the presence of remaining traces of tetranitromethane which, as already mentioned, are sufficiently unstable to withstand the highly sensitive Abel test.

The facts that a dilute alkaline boiling procedure causes a higher decrease in nitrogen content as well as a higher stability are attributed to two reasons. In the first place, alkaline hydrolysis is more rapid and more effective than acid hydrolysis which leads to a more rapid fall in nitrogen content. Secondly, boiling in dilute alkali decomposes nitrated oxidation products formed from the oxidizing action of tetranitromethane, while boiling in dilute acid does not. Thus, both these effects show that boiling in alkali produces the desired stability more efficiently than when the medium is acid.

The physical structures of the nitrates of amylose, amylopectin and the parent substance starch play an important role in stabilization treatment. Amylose nitrate, like the parent substance amylose, possesses a simple regular crystalline micellar structure and impurities in this structure are able to diffuse out easily. However, branching in the giant molecules of amylopectin nitrate tends to hinder diffusion, and the impurities are so hopelessly entangled that their rate of diffusion out of the structure is very slow. Due to this structural difference, amylose nitrate is inherently more stable than amylopectin nitrate, and the parent substance starch nitrate thus possesses a medium stability.

The causes of instability of nitrated starch or of its fractions are partly due to the formation of sulphonic acid esters when nitrating with mixed acid. The instability is much less when sulphuric acid is not present in the nitrating acid. Very long boiling (up to 150 hours) brings about increased stability by hydrolysis of such sulphonic acid groups. In our case, the nitrating medium is composed of nitric acid and acetic anhydride, and though sulphuric acid is absent, mere washing is not sufficient to bring about the desired stability because of the formed tetranitromethane. However, a relatively short boiling (4 hours) produces the desired stability since tetranitromethane is easily steam distilled in comparison with the hydrolysis of sulphonic acid groups.

Other organic solvents are described to have a stabilizing action on nitrated starch and its components. Thus, Ashford, et al. (78, 79) stabilized nitrated starch and its fractions prepared by mixed acid by treatment with alcohol. Both alcohol soluble and insoluble fractions are stabilized as a result of the ethanol treatment, and both amylose fractions possess more stability than the corresponding amylopectin fractions.

Nitrated starch, amylose, and amylopectin which are prepared by a mixture of nitric acid and acetic anhydride behave in a similar way. In all cases extraction with alcohol increases stability of both fractions, the insoluble fraction always being the more stable, and the stability of either the soluble or the insoluble fractions decreasing from amylose to whole starch to amylopectin. The inference of increased stability is not a simple matter to discuss and more data is necessary to justify it. The alcohol treatment causes a high increase in the Abel values, a result which is not attained by ordinary water boiling. One explanation for this, is that all traces of tetranitromethane are completely removed since it is known to be soluble in alcohol.

This interpretation of stabilization results tends to lead to the conclusion that the instability of nitrated starch, amylose, and amylopectin is a matter of practical manipulations rather than an inherent property possessed by these esters.

Part IV

EXPLOSIVE PROPERTIES OF STARCH NITRATES

A. THEORETICAL

1. Introduction

Nitrostarch is manufactured and used in the United States but has not found any favour in other countries (88). During World War I, certain explosives having nitrostarch as a base were used under the designations "Trojan grenade explosive", "Trojan trench mortar shell explosive" and "Gernite". These explosives were frequently referred to as "nitrostarch", but it should be noted that pure nitrostarch was not used alone as a military explosive. The nearest approach to it for military purposes is Gernite, which contains about 95 % nitrostarch, the balance being a binding material added for granulating purposes. The two Trojan explosives, which were practically identical in composition, contained approximately 25 % nitrostarch with inorganic nitrates and small amounts of materials added for stabilization, the reduction of both sensitivity and hygroscopicity, and the neutralization of possible acidity. The composition of Trojan explosive is as follows:

	Not less than %	Not more than %
Nitrostarch	23.0	27.0
Ammonium nitrate	31.0	35.0
Sodium nitrate	36.0	40.0
Charcoal	1.5	2.5
Heavy hydrocarbons	0.5	1.5
Antacid	0.5	1.5
Diphenylamine	0.2	0.4
Moisture	---	1.2

The composition of Gernite is as follows:

	Not less than %	Not more than %
Nitrostarch	95.5	98.25
Petroleum oil	0.75	2.00
Gum arabic	0.75	2.00
Moisture	----	1.00

The nitrostarch explosives were developed and used because when the United States entered World War I, a definite shortage of TNT supply was indicated and investigation showed nitrostarch explosives to be entirely suitable for trench warfare purposes and to offer an advantage of low cost and ample supply of raw material.

Pure dry nitrostarch is more sensitive to impact than TNT but less sensitive than dry guncotton or nitroglycerin. It is highly inflammable, being readily ignited by the slightest spark such as may result from friction, and like black powder burns with explosive violence.

Trojan explosives and Gernite were both much less sensitive than pure nitrostarch because they were required to pass the pendulum friction test of the U.S. Bureau of Mines and the rifle bullet test when packed in pasteboard containers. In heavy metal containers, these explosives frequently ignited and burned when penetrated by a rifle bullet, and in rare instances exploded under this test. Trojan explosive was especially insensitive to ignition, being rather difficult to ignite with the flame of a match when spread out unconfined. When once ignited in any quantity, however, it burned freely producing a light-colored smoke.

Pure dry nitrostarch as well as nitrostarch explosives were readily detonated by mercury fulminate detonators. A number 6 detonator containing one gram of fulminate composition will produce complete detonation unless the explosive had been rendered unduly insensitive by absorption of excessive moisture or by other causes.

The Trojan nitrostarch explosive was used as the bursting charge for hand grenades, rifle grenades, and trench mortar shells. It was well adapted to such purposes but was not considered for use as a bursting charge for high-explosive gun shells because it was too sensitive to setback. Its physical consistency was such that it was loaded into grenades through the small filling hole by means of vibrating machines, the explosive being jarred into the grenade through a small funnel opening. Trench mortar shells were loaded by hand stemming.

Gernite was used only for grenades and was considered too senstive for use as a trench mortar shell explosive. Being granular and free running it was readily loaded into the grenades through funnel openings, no attempt being made to pack it to a high density.

Nitrostarch has been considered for the manufacture of smokeless propellent powder and numerous attempts have been made to develop a satisfactory powder of this type, but the problem cannot as yet be considered solved. Nitrostarch explosives similar to Trojan grenade explosive have been used for a considerable number of years as blasting explosives for use in mining and quarrying, as well as other engineering operations. They have had considerable success as substitutes for the more expensive nitroglycerin explosives.

After thorough investigation there has recently been adopted a nitrostarch demolition explosive to serve as a substitute for TNT. Its composition is as follows (89).

TNT m.p. 79°	15.5
Nitrostarch 12.85 % N	34.5
Barium nitrate	43
Aluminium powder	5
Charcoal	2

This explosive is somewhat similar to that used during World War I, but the formula has been modified by raising the nitrostarch content and by replacing the ammonium nitrate with barium nitrate. It can be consolidated into blocks in the same manner as TNT, and in comparison tests it has been found that the TNT formula for computing small charges is directly applicable to the nitrostarch demolotion explosive.

2. Review of literature

2.1 Pure nitrostarch

Earlier workers observed that "xyloidine" is readily combustible, igniting over 150° C, and burning with very considerable violence leaving practically no residue. Berthelot (90) reported that the amount of heat evolved by the combustion of one acid equivalent of xyloidine is + 12.4 Cal.

2.1.1 Speed of detonation

Berthelot (91) found that the velocity of propagation of detonation in nitrostarch when placed in a tube made of tin at a density of 1.2 is 5210 to 5680 meters per second, provided that the exterior diameter of the tube is 4 mm. If the exterior diameter is increased to 5.5 mm., the corresponding speed becomes 5807 meters per second. In a tube made of lead of exterior diameter 4 mm. and at densities of 1.1, 1.2, and 1.35, the corresponding velocities are 4885, 4952, and 5512 meters per second, respectively.

Hackel and Urbanski (92) measured the spead of detonation of nitrostarch by the D'Autriche method. They used iron tubes having an internal diameter 34 mm. and an external diameter 38.6 mm. The nitrostarch is loaded at a density of 0.88 ± 0.04, and detonated by a number 8 detonator. Samples of nitrostarch ranging in nitrogen content from 13.43 to 8.89% gave the results in table 27.

Table 27

Nitrogen content	Speed of detonation m./sec.	Nitrogen content	Speed of detonation m./sec.
13.43	6190	11.62	3880
13.09	5740	11.02	3020
12.81	5300	10.51	2880
12.41	4950	9.44	1500
12.12	4480	8.89	1000

Le Roux (89) found the speed of detonation of a pure dry starch nitrate having 13.52 % nitrogen to be 4970 meters per second. He conducted the determination using the D'Autriche method in carton tubes having a diameter of 30 mm., at a density of 0.90.

2.1.2 Power

Hackel and Urbanski (92) measured the power of samples of nitrostarch varying in the percentage of nitrogen from 13.43 to 8.89 using the Trauzl lead block expasion test. They obtained the results given in table 28.

Table 28

Nitrogen content	Expansion cc.	Nitrogen content	Expansion cc.
13.43	430	11.62	300
14.09	395	11.02	260
12.81	375	10.51	230
12.41	360	9.44	160
12.12	320	8.89	125

Ashford, Cooke, and Hibbert (78) studied the explosive power of the ethanol insoluble fraction of starch nitrate. The net expansion in the Trauzl lead block is 358 cc. while that caused by TNT is only 256 cc.

Le Roux (89) conducted the Trauzl lead block test with a starch nitrate constaining 13.52 % of nitrogen. The expansion caused by 12.3 grams is 524 cc., and that caused by 12.5 grams is 556 and 533 cc.

2.1.3 Brisance

Hackel and Urbanski (92) studied the shattering effect of samples of nitrostarch containing from 13.43 to 8.89 % of nitrogen. They conducted the tests in a Kast brisance meter using copper cylinders 10.5 mm. in height and 7.0 mm. in diameter. Their values of copper cylinder compression are given in table 29.

Table 29

Nitrogen content	Compression mm.	Nitrogen content	Compression mm.
13.43	2.05	11.62	0.86
13.09	2.03	11.02	----
12.81	1.86	10.51	0.48
12.41	1.53	9.44	0.24
12.12	1.14	8.89	no detonation

2.1.4 Sensitivity to direct impact

Hackel and Urbanski (92) determined the sensitivity to direct impact of samples of starch nitrate containing 13.43 to 8.89 per cent of nitrogen. They used 2, 5, and 10 kilograms of falling weights to determine the minimum height that causes explosion of nitrostarch and calculated the mean work necessary to cause explosion. Their results are given in table 30.

Table 30

Nitrogen content	Minimum height in mm.			Work kg.m.
	2 kg.	5 kg.	10 kg.	
13.43	300	210	---	0.825
13.09	410	230	---	0.985
12.41	590	360	---	1.490
12.12	600	380	---	1.550
11.62	850	700	290	2.700
11.02	over1000	over1000	340	3.400
10.51	over1000	over1000	550	5.500
9.44	over1000	over1000	700	7.000
8.89	over1000	over1000	850	6.500

Ashford, Cooke, and Hibbert (78) determined the sensitivity to direct impact of the ethanol insoluble fraction of starch nitrate in comporative tests with TNT. Fractions containing 13.43 % and 13.96 % nitrogen showed a sensitivity 3.46 and 2.76 times greater than that of TNT, respectively.

Le Roux (89) found that a one kilogram drop causes starch nitrate containing 13.52 % nitrogen to explode 40 % of the time from a height of 500 mm., 48 % of the time from a height of 560 mm., and 60 % of the time from a 600 mm. height. He concluded that the energy of shock producing an explosion 50 % of the time is 0.56 kg.m.

2.1.5 Sensitivity to initiation by mercury fulminate

Le Roux (89) found that pure dry nitrostarch containing 13.52 % of nitrogen when compressed to a density of 0.90 could not be detonated by a detonator containing 0.25 gram of mercury fulminate. However when the detonator charge is increased to 0.30 gram a hight order detonation is produced.

2.2 Compositions containing nitrostarch

In the late decades of the niniteenth century, long after Braconnot's discovery of xyloidine, a tremendous number of investigators were occupied in developing improvements in the explosive properties of compositions containing nitrostarch as a base.

2.2.1 Ignition compositions

Trevorrow (93) patented a composition of matter comprising nitrostarch which is suitable for the preparation of ignition devices. The object of this composition is the provision of material having desirable viscosity characteristics and having no tendency to jell. The composition is formed by adding to a lacquer of nitrostarch in butyl acetate and benzene, an antijelling agent as acetonyl acetone in the proportion of 1 to 20 %. To this mixture a nitrophenol ignition compound is added.

2.2.2 Propelling compositions

Davey (94) claimed the use of nitrostarch as a component in propellants a century ago. The propellents consist of an intimate mixture of nitrostarch and the ordinary igredients of gunpowder.

Newton (95) patented a mixture suitable for use as a propellant for projectiles. For firearms, an excellent explosive is obtained by dissolving 20 to 30 parts of nitrated pulped cotton in 100 parts of nitroglycerin and 20 parts of camphor. To this mixture 100 parts of nitrostarch containing about 12 to 12,5 % of nitrogen and 200 parts of nitrodextrin of the same nitrogen content are added. The composition can be improved by the addition of oxygen yielding salts.

Schückler (96) patented a smokeless gunpowder which consists of a mixture of xyloidine, picrate, or chlorate of potassium, organic resins, nitronaphthaline, carbon, and mineral salts such as the nitrates of potassium, sodium, barium, or ammonium. A mixture containing 50 parts xyloidine, 40 parts saltpetre, and 5 parts nitrobenzone, gives a smokeless gunpowder of a medium power. He patented also a smokeless gunpowder comprising 5 to 10 percent of nitrobenzene and 95 to 90 per cent of nitrostarch.

Hengst (97) prepared an absolutely water proof and smokeless powder by milling nitrostarch with 3 % potassium nitrate, 1 % zinc sulphate, and 3 % wood charcoal. To this mixture is added a mixture of nitroglycerine, acetone, and linseed oil to form a thick homogeneous paste.

Pulverfabrik Hasloch a.M., Schmidt and Büttner (98) patented a process for the preparation of a smokeless propellant powder. The process consists in mixing 1 part of starch with 2 parts of nitrocellulose, and then adding the mixture to concentrated nitric acid. The nitrocellulose remains suspended in solution while the starch dissolves forming nitrostarch. By the addition of sulphuric acid or water, the nitrostarch is then precipitated on the suspended nitrocellulose.

King and **Lindsley** (99) patented a smokeless powder for use in fire arms. Their composition consisted of 52.50 % salpeter, 10.50 % charcoal, 12.50 % nitrocellulose, 7 % sulfur, 6.25 % nitrostarch, 6.25 % nitrosugar, 4 % oil of mirbane, and 1 % asphalt.

Snelling (100) patented a process whereby, 85 parts of nitrostarch containing 12.5 % nitrogen are mixed with 15 parts of liquid TNT. Only slight gelatinization is effected, the liquid TNT merely being spread over the surface of the nitrostarch granules. The mixture is then heated for about 15 minutes to a temperature above 80° C and is thus converted into a tough colloidal mass which is suitable for use as smokeless powder. The mass burns with hight uniformity and is sufficiently tough to withstand the high pressures in guns without breaking up or producting erratic ballistic results.

2.2.3 Detonating compositions

Waller (101) inviteda nitrostarch composition suitable for use as the main charge of a detonating cap or electric detonator. A mixture made up of 80 % nitrostarch, 5 % diphenylamine, and 15 % potassium chlorate forms a satisfactory composition. This nitrostarch composition is utilized as the secondary charge in a reenforced detonator of the usual type, i.e. mercury fulminate or some other suitable initial detonating agent. The average size of the nitrostarch grains is greater than 0.045 mm. so that the composition will possess a relatively free flowing character and can be loaded by detonator loading devices.

2.2.4 Boosting compositions

Snelling (102) prepared a nitrostarch composition suitable as booster charge for shells and torpedoes. For the purpose of a booster explosive, a material must be highly explosive and have great strength, and at the same time be sufficiently insensitive to withstand the heavy shock of setback in the gun. Booster charges have usually consisted of compressed pellets of tetryl or TNT. These substances have the ability of consolidating from pulverulent form to yield hard and dense tablets of suitable sensitiveness when compressed under a pressure of 5000 pounds per square inch or higher. While nitrostarch is sufficiently powerful for use as a booster charge, it is too sensitive for this purpose in its ordinary condition, since it would explode prematurely from the shock of powder gases on the base of shell. Ordinary nitrostarch is also unsatisfactory for use as a booster explosive because of its pulverulent nature. It cannot be consolidated, even with pressures much in excess of those employed in forming pellets of tetryl or TNT. In fact, no pressures employed have proved sufficient to cause nitrostarch to unite to form a firm pellet, such as is required in booster charges. Snelling claimed that when nitrostarch is blended with a suitable agglomerating and desensitizing agent, it is capable of forming a booster explosive superior to either tetryl or TNT. As agglomerating agents, paraffin hydrocarbons, beeswax, ceresin, or rosin in the proportion of 1 to 10 % are used, and 2 % heavy mineral oils are incorporated as desensitizing agents. An oxidizing agent such as ammonium nitrate may also be incorporated. The agglomerated and desensitized material is then compressed into pellets under a pressure of 1000 pounds per square inch.

2.2.5 High explosive compositions

During World War I nitrostarch military explosives were developed, and a detailed discussion of their use as military high explosives was already given in the introduction to this part. Little development was undertaken after World War I.

Gillespie (103) invented a desensitized nitrostarch composition suitable for filling grenades. A composition having sufficient strength to fragment the metallic envelop of a grenade and drive the fragments at a high velocity to a maximum range is composed of 97.25 % nitrostarch, 1.25 % heavy lubricating petroleum oil, 1.00 % gum arabic, and less than 0.50 % water. This composition is not exploded by a rifle bullet, is free running which permits easy loading into holes, withstands humidity, and can be easily detonated by one gram of fulminate-chlorate composition.

Snelling (104) patented a nitrostarch composition having great strenght and which is insensitive to blows or friction. This combination of properties is essential in military explosives used as filling charges in drop bombs and sea mines. Insensitiveness to blow or friction is attained by incorporating a hygroscopic material such as ammonium nitrate or dextrose. An explosive possessing exceptional schattering strength is composed of 60 to 75 % nitrostarch, and 25 to 40 % of a solution of ammonium nitrate in water. Another composition contains nitrostarch in varying proportions, a nitrate or chlorate as an oxygen carrier, and heavy lubricating oil as a desensitizing agent. He patented an explosive suitable for filling shells comprising 40 % nitrostarch, 57 % lead nitrate, and 3 % oil.

Young (68) reported that some nitrostarch explosives are entirely satisfactory and suitable substitutes for TNT as demolition explosives with respect to sensitivity, power, reliability and ease of detonation, hardness and resistance to crumbling, suitability for use in bangalore torpedos, and use under water. The only important respect in which nitrostarch demolition explosives may suffer appreciably in comparison with TNT is instability during long storage. However, unqualified approval by the U. S. Ordnance department has been given to nitrostarch as an emergency explosive and for peacetime use involving storage of not more than a few years.

Snelling (105) invented a very powerful, highly shattering, military demolition explosive suitable for breaking a standard railroad rail without stemming. Its composition consists of at least 20 % nitrostarch mixed with an equal part of TNT, an oxygen carrier such as barium nitrate in the proportion of 40 %, in addition to small percentages of fine aluminum flakes to increase the energy, dicyandiamid to improve stability, coal dust, graphite, and paraffin.

2.2.6 Commercial explosive compositions

Dittmar (106) patented the use of a nitrated mixture of pulp and starch as the best adapted substance to be combined with nitroglycerin in dynamites.

Steele (107) produced an absolutely safe explosive, being unaffected by moisture, ordinary blow, shock or friction. One composition consists of a mechanical combination of nitrostarch and an oxygen carrier such as potassium chlorate or permanganate. In a second composition, nitrostarch is mixed with ammonium nitrate in the presence of alcohol. From 1 to 5 % of powdered aluminum also may be added to the mixture.

He also patented a plastic explosive which is more particularly adapted for charging overhead holes in mines and underground work. Its preparation consists of mixing nitrostarch with an oxidizing agent in the presence of alcohol and castor oil.

Holmes (108) prepared an improved pulverulent water proof composition consisting of 30 parts sodium nitrate, 10 parts nitrobenzene and 60 parts nitrostarch. It is also possible to substitute nitroglycerin for the nitrobenzene.

Braunstein (109) patented a blasting powder in which the explosive base undergoes complete combustion. The composition consists of a mixture of nitrostarch and finelly divided iron fillings in the proportion of 79 % to 40 % . Ammonium nitrate can also be added.

He also prepared an improved nitrostarch blasting powder by reducing its temperature of explosion. This effect is brought about by decreasing the oxidizing ingredients. A suitable composition contains 25 % nitrostarch, 45 % calcium carbonate, 30 % sodium nitrate with a small percentage of an oil to give consistency, and a stabilizing agent.

He also produced a plastic explosive with greatly increased strength and brisance. Increasing the rate of detonation by elimination of films of air between nitrostarch particles is accompolished by helding the latter elastically in a viscous ground mass forming a continuous medium of incompressable nature. A suitable ground mass is glucose, in the proportion of 5 to 12 %, which does not colloid or desensitize nitrostarch.

Lezinsky (110) patented an explosive suitable for use in underground work. The explosive consists of a homogeneous mixture of nitrated starch and resin mixed with potassium chlorate or some other oxygen yielding substance.

Nathurst (111) invented a glatin explosive that normally will be plastic, non-freezing, and will not produce noxious gases on detonation. The explosive consists of gelatinizing 6 parts nitrostarch containing about 12.75 % nitrogen and five parts nitrocellulose containing 12.25 % nitrogen in 70 parts of nitroglycerin. Then 18 parts of ammonium nitrate and one part of antiacid are added to the gelatinized mass.

Peters (112) invented a safety powder for blasting. It consists of the following ingredients mixed to homoginity: ammonium nitrate 75 %; nitrostarch 20 %; and a solution of four parts of mirbane oil and one part of asphalt 5 %.

Bronstein and Waller (113) patented several oxygen balanced nitrostarch compositions, improving their use as detonating explosives. A fused mixture of 10 to 30 % ammonium nitrate and 10 to 30 % TNT is mixed with 30 to 45 % nitrostarch and 45 % of barium nitrate. The barium nitrate may also be substituted in part by sodium nitrate. To this mixture is then added less than 10 % of sulphur and smaller amounts of carbonaceous material, calcium carbonate, and paraffin oil, zinc oxide and mineral oil are also added in small percentages.

Treese (114) patented a blasting explosive consisting of 13 % yellow wax, 7 % soap stock, 21 % sulphur, 11% niter, 22 % potassium chlorate, and 26 % nitrostarch.

Waller (115) prepared a grangular uncompressed explosive suitable for the use in blasting and having good water resisting properties. Its composition consists of 10 % nitrostarch, 73 % sodium nitrate, 7.5 % sulphur, 7.5% charcoal, 1 % calcium carbonate, and 1 % dried starch paste. If mononitronaphthalene is added, inflammability is reduced. A typical explosive of this latter type consists of 20 % nitrostarch, 51 % sodium nitrate, 20 % ammonium nitrate, 7 % mononitronaphthalene, 1 % paraffin oil, and 1 % calcium carbonate. Ammonium nitrate may by increased to 60 % accompanied by elimination of sodium nitrate and the addition of about 5 % sulphur. A third composition of high brisance and noninflammibility is composed of 65 % nitrostarch, 15 % water, and 20 % ammonium nitrate or an ammonium nitrate calcium nitrate mixture.

Olsen (116) formulated an explosive suitable for ordinary blasting. Trojan grenade or mortar shell powder is mixed with a propellant powder such as smokeless powder to form the detonating explosive.

Snelling (117) reduced the water content of wet nitrostarch by mixing it with a concentrated solution of ammonium nitrate. The excess water is then removed by centrifugation. An explosive may then be prepared by the addition of sodium nitrate, ammonium perchlorate or any other oxidizing salt. Snelling also sensitized ammonium nitrate explosives by the use of nitrostarch. Thus, while ammonium nitrate explosives sometimes fail to detonate completely with the usual TNT booster charge when used in blasting soft rock, complete detonation results when the granules of explosive are coated with 0.5 to 3.0 % of starch nitrate.

Rupp (118) patented a composition consisting of nitrostarch and an oil acting as a dust reducing agent. The mixture consists of 35 % nitrostarch, 10 % ammonium nitrate, 54.50 % sodium nitrate, 0.20 % zinc oxide, and 0.30 % mineral oil.

Perrot, Gawthrop, and Taylor (119) sensitized ammonium nitrate with nitrostarch. They found that the addition of nitrostarch to ammonium nitrate in quantities of 1 % and higher increases its sensitivity to explosion at elevated temperatures when under confinement and increases completeness and speed of detonation when the mixture is detonated by a tetryl booster.

Wyler (120) prepared an artificial solid and infusible fuel from alcohol and nitrostarch. Several compositions were prepared containing about 60 % methyl alcohol, 10 % ethyl alcohol, 10 % water, 10 % nitrostarch, and in some cases formaldehyde. He also invented a light fluffy pulverulent mixture suitable for use as an explosive. It consists of a solid solution of at least 8.4 % nitrostarch in nitrated sucrose.

Cairns (121) invented a colloided nitrostarch-TNT explosive. It can be prepared by adding a mixture of 8.5 parts of nitrostarch and 1.5 parts of ethyl alcohol to 10 parts of TNT and then allowing the mass to dry at room temperature. The dried mixture is then heated to 80 to 95^{o} C until colloided and cooled to form a fine-grained homogeneous explosive.

2.2.7 Explosive properties of nitrostarch compositions

Swenehart (122) tested a land clearing nitrostarch mixture for detonation, sensitiveness to impact by rifle bullet, explosion by sympathy, inflammability, resistance to moisture, effect of moisture on detonation and efficiency in use, effect of temperature and toxic effect. The tables of data on stump clearing from the use of this explosive and that of a 20 % ammonia dynamite are given with the statement that "No definite inference should be made other than that the nitrostarch explosive gives comparatively effective results."

Schrimpff (123) reported that nitrostarch explosives are classified into two classes in the United States, according to the percentage of nitrostarch they contain. An example of class I is an explosive containing 50 % nitrostarch, 47.5 % sodium nitrate, 1.5 % oil, and 1 % sodium bicarbonate. An example of class II contains 15 % nitrostarch, 73 % ammonium nitrate, 3 % TNT, 2 % coal dust, 6 % aluminum, 0.5 % mineral oil, and 0.5 % zinc oxide. The proporties of the two classes are summarized in table 31.

Table 31

Properties	Class I	Class II
Speed of detonation m/sec	4200	4150
Self excitation in cm. 32 mm. diameter of cartridges	5	7.5
Trauzl expansion cc. 2 gram detonator	259	400
Hess lead cylinder compression mm. 62.5 mm hight and 37.5 mm diameter	17	16

Urbanski, Hackel, and Kwiatkowski (124) examined the explosive properties of nitrostarch-ammonium nitrate and nitrostarch sodium nitrate mixtures. They found that the explosive force varies within wide limits according to the quantity of nitrostarch in the mixture.

Young (68) investigated nitrostarch demolition explosive and TNT in comparative tests. His results are sumarized in table 32.

Table 32

Properties	Nitrostarch	TNT
Hygroscopicity	1.79 %	negligible
Explosion temperature	410° F	870° F
Sensitivity to impact		
2 kg. weight, minimum height in inches	8	16
rifle bullet, iron pipe bomb	usually burns	occasionally burns
rifle bullet, ordinary package	negative	negative
Sensitivity to flame		
ignition by black powder fuse	burns	negative
Sensitivity to friction		
pendulum friction steel shoe	snaps	negative
pendulum friction fiber shoe	negative	negative
Power TNT 100 %	88	100
Density in block form	1.78	1.46

Le Roux (89) examined the explosive properties of Trojan, Gernite, and Nitrostarch explosives. His results are summarized in table 33.

Table 33

Properties	Gernite	Trojan	Nitrostarch
Density	0.90	1.20	1.45
Sensitivity to initiation by mercury fulminate gm.	0.3 d. 0.9	0.5 d. 1.2	0.3 d. 1.45 or 1.5
Speed of detonation m/sec. in carton tubes 30 mm. diam.	d. 0.9 5050	d. 1.2 3220	d. 1.50 4570 d. 1.60 4700 d. 1.70 4900 d. 1.75 4940 d. 1.80 5130 d. 1.87 5420
Trauzl lead block expansion cc.	13.3 gm. 533 13.3 gm. 558 13.1 gm. 536	18.8 gm. 590 17.2 gm. 515 18.2 gm. 560	17.6 gm. 560 17.6 gm. 560 17.6 gm. 561
Impact sensitivity 1 kg. drop in meters	0.56 48 %	0.70 48 %	0.85 50 %

B. EXPERIMENTAL

3. Sensitivity characteristics (125)

The ease with which explosives detonate on receiving a sharp blow or shock is of practical importance in determining manufacturing precautions and safety in handeling, and also in deciding what initiators can be used. Sensitivity tests evaluate either potential hazards such as friction and impact, or resistance to initiator impulse. In a technical sense, the sensitivity of an explosive is not a unique and accurately definable quantity. In practice, sensitivity is a relative term and is considered in a qualitative sense as the degree of susceptibility to initiation by some stimulus encountered in usage compared to some arbitrary standard. In laboratory tests it is customery to set up arbitrary but standardized conditions and to test a number of explosives under such parameters. The criterion for relative sensitivity is then usually measured in terms of the total energy of the stimulus without regard to losses or rate of application such energy.

3.1, Sensitivity to direct impact

The impact sensitivity of an explosive, under specific conditions, is determined by the magnitude and rate of application of a compressive pressure necessary to produce initiation of detonation or deflagration. The impact sensitivity depends on the mechanical properties of the sample as well as the chemical stability of the explosive.

In practice, only the relative impact sensitivity is measured. Usually the impact is produced by a falling weight or a high velocity projectile and the sensitivity is expressed in terms of the energy of the weight or projectile necessary to produce initiation of detonation or deflagration. Results vary markedly, depending on the nature and area of the striking surfaces, rate of application of energy as opposed to the total energy involved, and physical configuration of the sample.

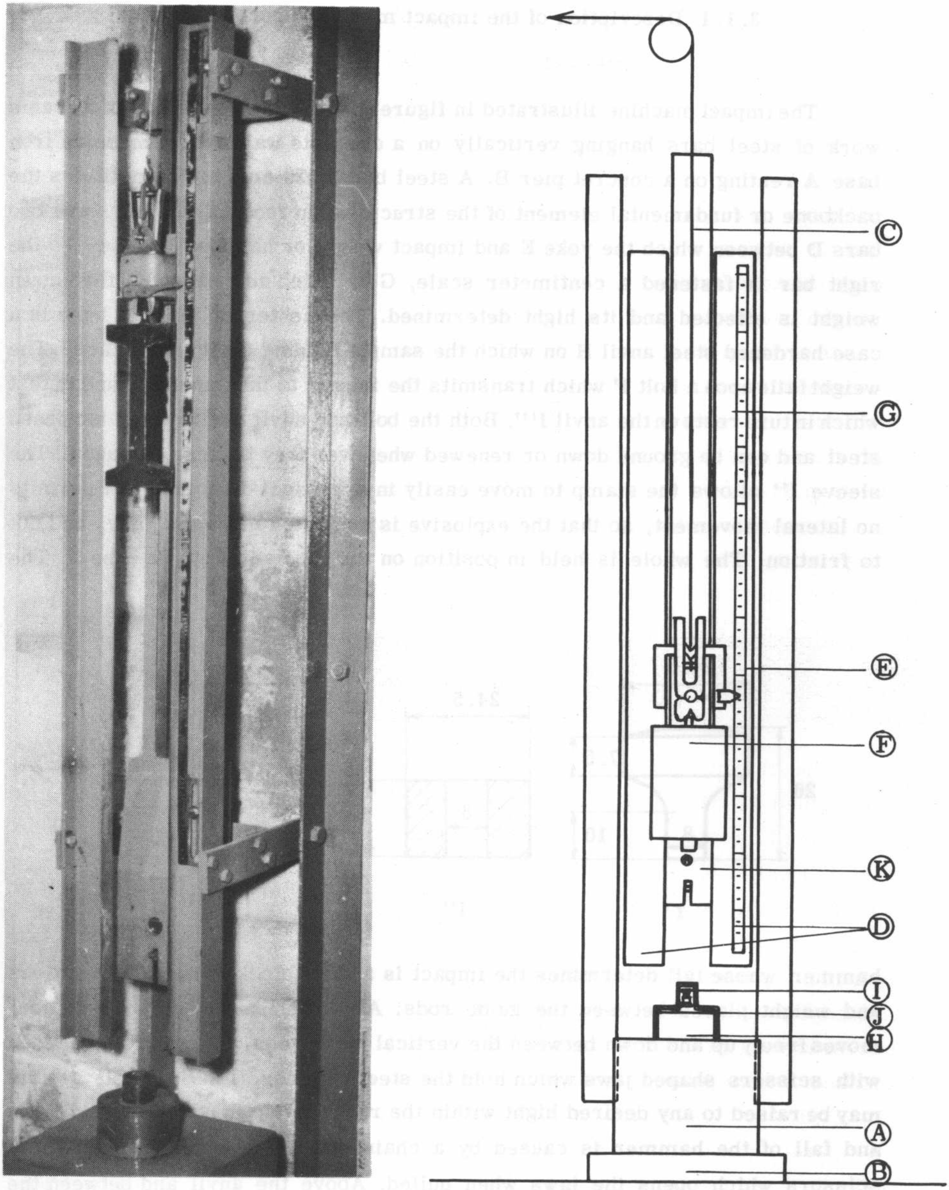
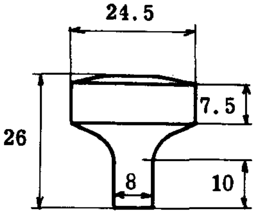


Figure 46 Oerlikon impact machine
(Courtesy Oerlikon Machine Tool Works-Buehrle & Co. Zurich)

3.1.1 Description of the impact machine (Oerlikon type)

The impact machine illustrated in figure 46 consists essentialy of a frame work of steel bars hanging vertically on a concrete wall over a massive iron base A resting on a concret pier B. A steel bar C 120 cm. high constitutes the backbone or fundamental element of the structure. In front of this bar, are two bars D between which the yoke E and impact weight or hammer F move. To the right bar is fastened a centimeter scale, G by which adjustment of the known weight is effected and its hight determined. The center of the iron base is a case hardened steel anvil H on which the sample holding device I is placed. The weight falls upon a bolt I' which transmits the impact to the explosive under test which in turn rests on the anvil I'''. Both the bolt and anvil are made of hardened steel and can be ground down or renewed whenever they become damaged. The sleeve I'' allows the stamp to move easily in a vertical direction, but permits no lateral movement, so that the explosive is subjected to impact only, and not to friction. The whole is held in position on the base anvil by the base J. The hammer whose fall determines the impact is a steel block of known dimentions and weight placed between the guide rods. Above the hammer is a yoke that moves freely up and down between the vertical guide rods. The yoke is provided with scissors shaped jaws which hold the steel hammer, and the whole system may be raised to any desired hight within the range of the machine. The release and fall of the hammer is caused by a chain attaced to the other end of the scissors which opens the jaws when pulled. Above the anvil and between the guide bars a device K is attached to the central bar which permits the hammer to strike the bolt once only avoiding damage to the latter.



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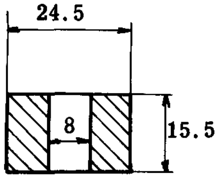

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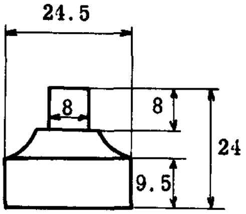

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Table 34

Explosive	Height in cm. of 2 kg. drop									
	20	30	10	50	60	70	80	90	100	105
	Percentage firing									
Amylose nitrate	-	10	15	15	15	55	50	60	60	-
Amylopectin nitrate	-	5	10	10	15	30	35	30	50	-
TNT	-	-	-	-	-	-	5	-	5	10
Hexogen	10	20	15	20	40	65	85	90	-	-

Table 35

Explosive	Energy of direct impact (kg. m) necessary to produce		
	10% explosions	50% explosions	90% explosions
Amylose nitrate	0.6	1.6	--
Amylopectin nitrate	0.9	2.0	--
TNT	2.1	-	--
Hexogen	0.4	1.3	1.8

3.1.2 Test method

The explosive is finely pulverized to pass 0.10 mm. screen and dried at 45°C. Then 15 ± 2.5 mgm. of the explosive are placed between the anvil and bolt and subjected to a 2 kg. pressure for one minute. Twenty five trials are conducted at each of the following distances:

20, 30, 40, 50, 60, 70, 80, 90, 100 cm.

and the percentage explosions in each case calculated.

3.1.3 Test results

The results of comparative tests of amylose nitrate 13.37% N, amylopectin nitrate 13.25% N, TNT, and hexogen are given in tables 34 and 35.

3.2 Sensitivity to frictional impact

The frictional impact sensitivity is determined by applying a frictional impact type of stimulus to an explosive placed between an anvil and a bolt and subjected to the scraping action of the bolt while revolving at a constant speed. The measure of the test is the probability of occurance of ignition or detonation under standard conditions of frictional-impact stimulus as compared with other explosives.

3.2.1 Description of the frictional-impact machine (Oerlikon type)

The essential features of the frictional-impact device, illustrated in figure 47 are a vertical steel shaft A, capable of being revolved at a constant speed. A disc B to which any desired weight C may be added is fixed to the upper part of the steel shaft. To the lower end of the shaft a bolt D is fixed which revolves with the shaft and produces a frictional-impact stimulus to the explosive under test E, which in turn rests on the anvil F. Both the bolt and anvil are made of hardened steel and their surfaces are either plane or corrogated so as to produce maximum shearing stresses. The sleeve G allows the bolt to move easily in a vertical direction and the whole assembly is held in position by the base H. The machine is driven by a suitable motor mounted on a wooden base together with the assembly.

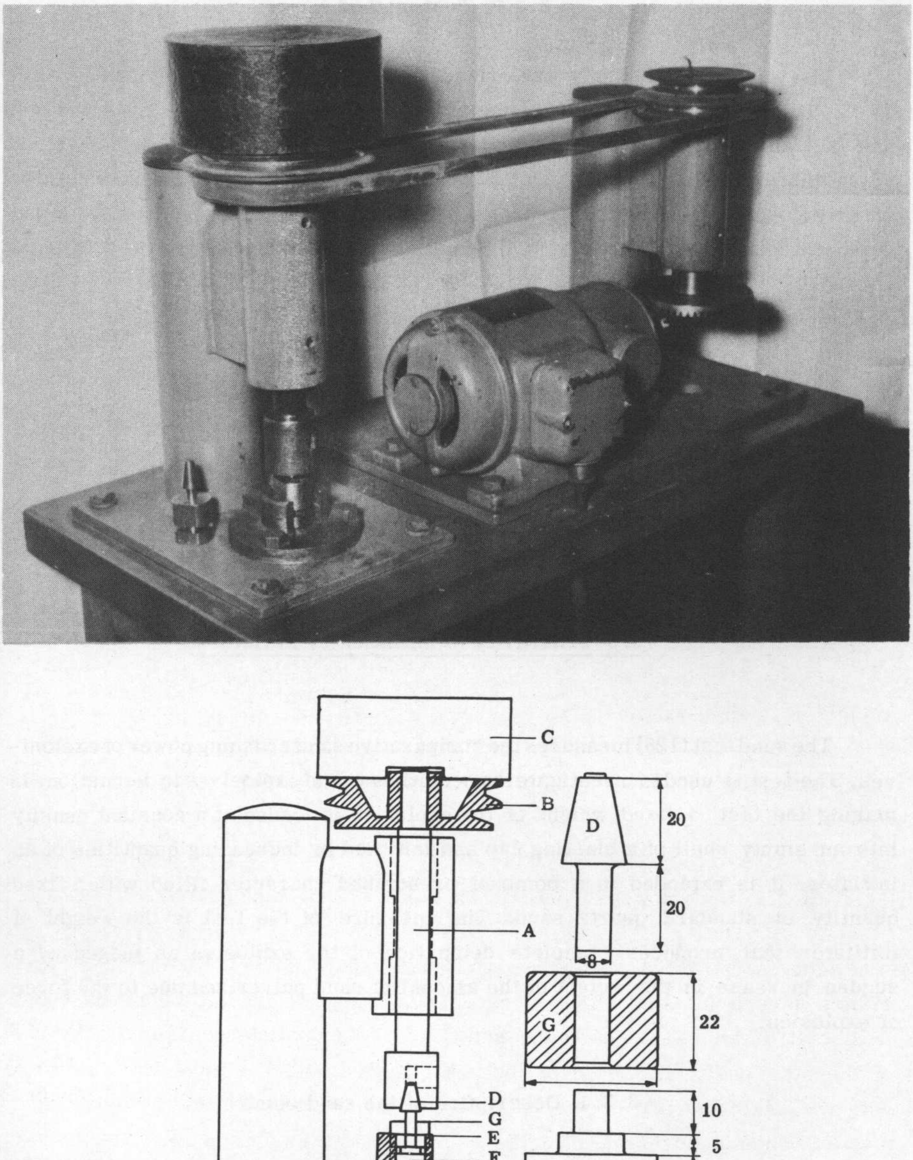


Figure 47 Oerlikon Frictional-import machine
(Courtesy Oerlikon Machine Tool Works Buehrle & Co. Zurich)

3.2.2 Test method

The explosive is finely pulverized to pass 0.10 mm. screen and dried at 45°C. Then 55 ± 5 mgm. of the explosive are placed between the anvil and bolt and 10, 20, or 30 kgm. weights are added to the disc. The machine is revolved 50 revolutions at a speed of 20 r.p.m. and the number of revolutions counted untill detonation occures. Five trials are conducted with each explosive in the pure state and when mixed with 10% quartz sand pulverized to pass 0.20 mm. screen.

3.2.3 Test results

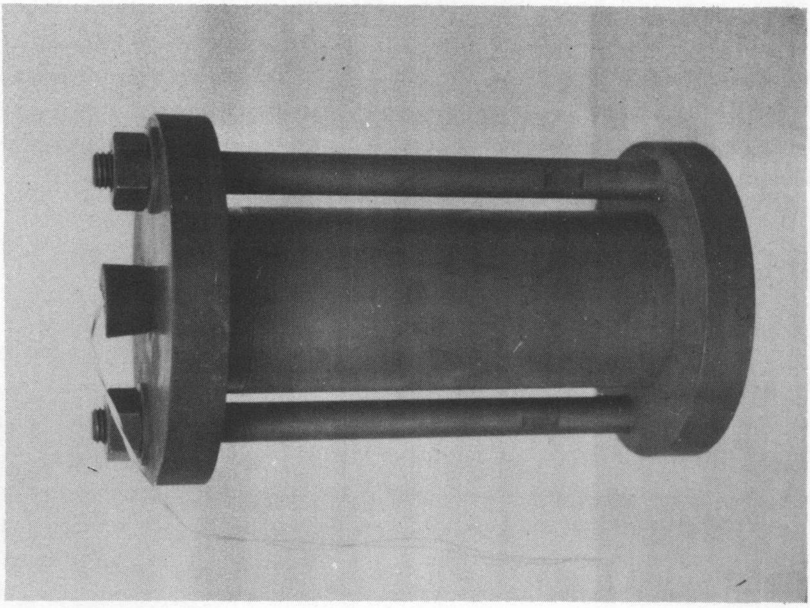
The results of comparative tests of amylose nitrate 13.37% N, amylopectin nitrate 13.25% N, TNT, Hexogen, and PETN showed no probalility of occurance of ignition or detonation even under the maximum shearing stresses applied.

3.3 Sensitivity to initiation by initiators

The sand test (126) measures the comparative sand crushing power of explosives. The test is used to investigate the sensitiveness of explosives to detonation. In making the test, a fixed weight of the explosive is loaded at a constant density into an empty shell of a blasting cap and initiated by increasing quantities of an initiator. It is exploded in a bomb of prescribed character filled with a fixed quantity of standard quartz sand. The measure of the test is the weight of inititator that produces complete detonation of the explosive as judged by a sudden increase in the weight of the amount of sand pulverised due to the force of explosion.

3.3.1 Description of the sand bomb

The sand bomb, illustrated in figure 48, consists of a small steel bomb 20.3 cm. long and 8.3 cm. in diameter, with a cylinderical chamber or cavity 16.5 cm. deep and 5.1 cm. in diameter. A cover having the same diameter



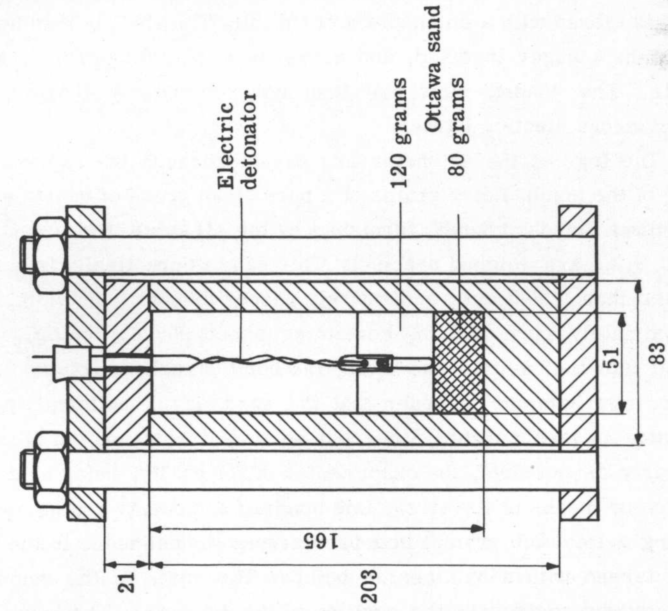


Fig. 48 U.S. Bureau of Mines Sand Bomb

as the bomb is 2.1 cm. thick at the edge and about 2.9 cm. thick at the center. The central thicker part provides a slight projection which just fits in the top of the cylinderical cavity of the bomb. Near the center of the cover two small holes are drilled which allow the legs of an electric detonator to fit snugly. A suitable clamping device, shown in the illustration, retains the cover in position and prevents loss of sand when the detonator is fired.

3.3.2 Test method

A 0.600 gram sample of the dry explosive is placed in an empty shell of a Nobel-Troisdorf No.8 aluminium detonator, 6.8 mm. external diameter, 6.2 mm. internal diameter, and 41.8 mm. high. A plunger 6.1 mm. in diameter is inserted in the shell and the explosive is pressed to the densities: 0.8, 0.9, and 1.0 gm/cc. Increasing amounts of initiating explosives (200 to 300 mgm. of mercury fulminate and 10 to 30 mgm. of lead azide), are weighed and added on the top of the pressed explosives in the shells. The latter is covered with a reenforcing cap having an internal diameter 5.1 mm., an external diameter 6.1 mm., a hight 7.3 mm., and having a hole 0.2 mm. in diameter at the top which is closed with a small piece of tin foil. The shell is then held in a loading block, the plunger inserted, and a pressure of 100 kgm/cm^2. applied for one minute. The loaded caps are then covered with a Nobel-Troisdorf instantaneous electric lighter.

The legs of the detonator are passed through the two small holes in the cover of the bomb. Forty grams of a pure clean grade of quartz sand designated as "Ottawa Standard Sand", furnished by the Ottawa Silica Co., of Ottawa, Ill., U.S.A., are weighed precisely. This sand is practically free form particles coarser than 0.840 mm. and entirely passes through 0.590 mm. screens. It is approximately pure quartz, containing about 99.90% of SiO_2. This sand is poured into the cavity of the bomb, the bomb struck sharply two or three times with a light hammer in order that the sand may be uniformly packed, and the detonator is then carefully inserted so that it rests on top of the sand and in, as nearly as possible, the exact center of the cavity, being held upright in this position by means of its wires. One hundred and twenty grams more of the sand (making a total 200 grams) is poured around the detonator in the bomb, and the latter tapped with a hammer as before. The cover of the bomb is then put in place without distrubing the position of the detonator. The bomb is then placed in the clamping device and held tightly in position by screwing down the hexagonal nuts on the upright iron rods. The detonator is fired with a small generator twist type blasting machine. After the explosion, the cover of the bomb is removed and the sand emptied on a large sheet of glazed paper, that adhering within the cavity being removed by means of a suitable brush. The electric detonator legs together with any large fragments of the aluminium shell are rejected after any adhering sand has been removed from them. The entire charge of sand is screened through a 0.590 mm. sieve for three minutes, and the material passing through is weighed.

3.3.3 Test results

The results of the sensitivity of amylose nitrate 13.37% N to initiation by mercury fulminate and amylopectin nitrate 13.25% N to initiation by lead azide are given in tables 36 to 41 and are graphically shown in figures 49 and 50.

3.4 Discussion of the sensitivity results

The following comments may be made on the results described in this section:

1. The minimum impact energy for zero up to ninety percent probability of detonation indicated that amylose and amylopectin nitrates are more sensitive to direct impact stimulus than TNT, and less sensitive than Hexogen. The minimum impact energy for 10% probability of detonation is 0.6, 0.9, 2.1, and 0.4 kg.m. respectively. From the point of view of practical hazard, the maximum impact energy for zero probability of detonation is 0.4 kg.m. for amylose and amylopectin nitrates, 1.4 kg.m. for TNT, and lower than 0.4 kg.m. for Hexogen.

These results agree well with what we know about sensitivity and oxygen balance. The oxygen balance values of Hexogen, amylose nitrate (13.37% N), amylopectin nitrate (13.25% N), and TNT are -21.6, -31.0, -31.5, and -74.0 respectively. This gradual decrease is in direct relation to impact energy values which were found for these explosives.

2. In contrast to direct impact tests, amylose and amylopectin nitrates, TNT, Hexogen, and PETN showed dead sensitivity to the frictional impact stimulus

applied. There is no tendency for these explosives, even PETN which is classified with initiating explosives, to adhere to the surfaces involved in the frictional impact, thus nullifying localized forces necessary to cause detonation.

3. The sensitivity of amylose nitrate to initiation by mercury fulminate is demonstrated in figure 49. The developed explosive power is independent of the magnitude of the initiating impulse, providing that the impulse is above a certain minimum. Furthermore, amylose nitrate is found to be a sensitive explosive to initiation. At 0.8, 0.9, and 1.0 loading densities, 220, 230, 240 milligrams of pure mercury fulminate are the minimum amounts necessary to initiate a complete detonation.

4. The sensitivity of amylopectin nitrate to initiation by lead azide is demonstrated in figure 50. Amylopectin nitrate is extremely sensitive to initiation by lead azide. At 0.8, 0.9, and 1.0 loading densities, only 22, 24, and 26 milligrams of pure lead azide are the minimum amounts necessary to initiate a complete detonation.

5. It is noted that both amylose and amylopectin nitrates loose their sensitivity to initiation when pressed to higher densities, as judged by an increase in the magnitude of initiating impulse applied to develop a complete detonation.

Table 36

Sensitivity of amylose nitrate loaded at a density of 0.8 gm./cc. to initiation by mercury fulminate

Wt. in mgm. of Mercury fulminate	Weight of sand in grams pulverized finer than 0.590 mm. by reenforced electric detonator containing 0.6 gm. of 13.37% N amylose nitrate					
	First trial	Second trial	Third trial	Fourth trial	Fifth trial	Mean
180	9.20	10.05				9.63
190	10.30	10.35				10.33
200	11.15	11.00				11.08
210	11.40	11.00				11.20
220	75.20	74.05	74.95	77.65	78.95	76.16
230	76.20	75.05	76.45	74.95	83.50	77.23
240	75.85	75.15	76.05	79.15	83.60	77.96
250	78.75	77.05				77.90
260	79.30	80.90				80.10
270	81.75	80.95				81.35
280	80.20	82.10				81.15

Table 37

Sensitivity of amylose nitrate loaded at a density of 0.9 gm./cc. to initiation by mercury fulminate

Wt. in mgm. of Mercury fulminate	Weight of sand in grams pulverized finer than 0.590 mm. by reenforced electric detonator containing 0.6 gm. of 13.37% N amylose nitrate					
	First trial	Second trial	Third trial	Fourth trial	Fifth trial	Mean
190	10.00	11.60				10.80
200	10.90	11.00				10.95
210	11.45	11.45				11.45
220	10.10	12.00				11.05
230	80.05	75.90	75.80	80.55	77.80	78.02
240	78.05	80.35	79.70	76.20	75.50	77.96
250	78.30	75.65	76.65	79.15	80.95	78.14
260	81.15	79.15				80.15
270	81.15	82.00				81.58
280	81.05	82.85				81.95
290	81.95	82.05				82.00

Table 38

Sensitivity of amylose nitrate loaded at a density of 1.0 gm./cc. to initiation by mercury fulminate

Wt. in mgm. of Mercury fulminate	Weight of sand in grams pulverized finer than 0.590 mm. by reenforced electric detonator containing 0.6 gm. of 13.37% N amylose nitrate					
	First trial	Second trial	Third trial	Fourth trial	Fifth trial	Mean
200	10.15	11.95				11.05
210	11.20	11.90				11.55
220	12.05	11.75				11.90
230	12.25	11.95				12.10
240	79.15	80.80	78.05	76.05	80.60	78.93
250	79.20	79.15	80.60	81.05	74.60	78.92
260	79.45	79.10	80.65	83.05	80.50	80.55
270	81.05	83.65				82.35
280	83.10	84.10				83.60
290	82.00	85.40				83.70
300	82.35	82.45	81.35	85.95	87.90	84.00

Sensitivity of amylose nitrate to initiation by mercury fulminate

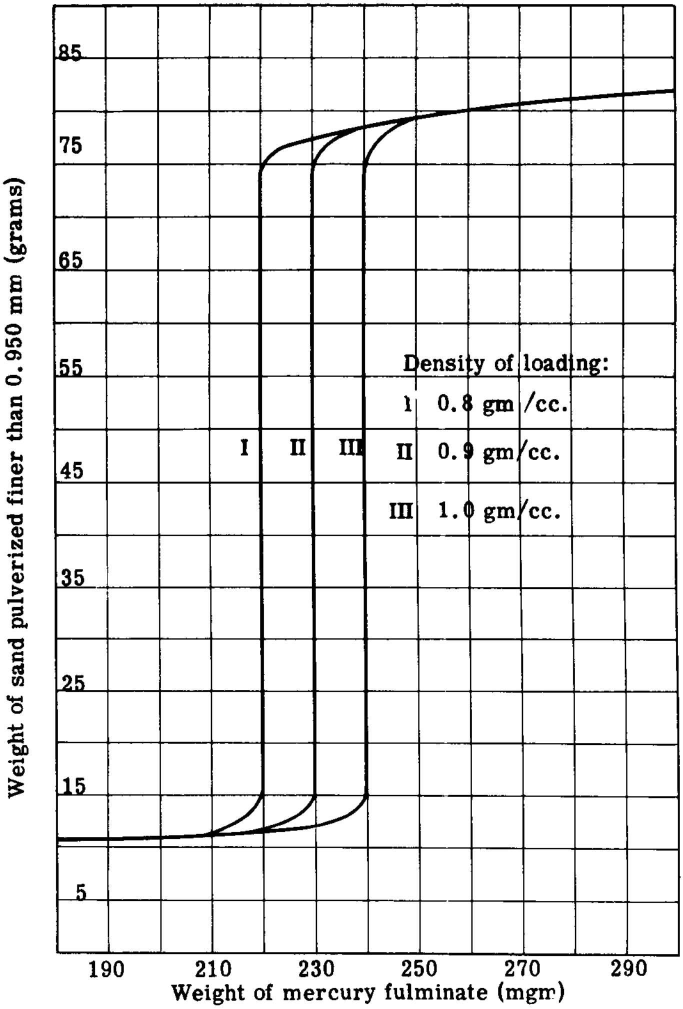


Figure 49

Table 39

Sensitivity of amylopectin nitrate loaded at a density of 0.8 gm./cc. to initiation by lead azide

Wt. in mgm. of Lead azide	Weight of sand in grams pulverized finer than 0.590 mm. by reenforced electric detonator containing 0.6 gm. of 13.25% N amylopectin nitrate					
	First trial	Second trial	Third trial	Fourth trial	Fifth trial	Mean
16	0.85	0.70				0.80
18	0.60	0.90				0.75
20	1.10	1.05				1.08
22	66.90	65.95	64.20	63.95	69.15	66.03
24	67.65	66.80	65.50	64.40	68.85	66.64
26	67.10	67.35	65.30	68.15	69.70	67.52
28	67.00	65.75				66.40
30	68.25	69.30				68.80
32	68.10	69.80				68.95

Table 40

Sensitivity of amylopectin nitrate loaded at a density of 0.9 gm./cc. to initiation by lead azide

Wt. in mgm. of Lead azide	Weight of sand in grams pulverized finer than 0.590 mm. by reenforced electric detonator containing 0.6 gm. of 13.25% N amylopectin nitrate					
	First trial	Second trial	Third trial	Fourth trial	Fifth trial	Mean
18	0.90	0.85				0.88
20	0.95	1.05				1.00
22	1.20	1.00				1.10
24	68.05	65.05	66.25	65.20	68.30	66.58
26	67.10	67.00	67.60	69.70	66.60	67.60
28	68.80	70.25	65.65	66.25	70.10	68.21
30	70.35	71.00				70.70
32	70.50	70.95				70.75
34	71.90	72.00				71.95

Table 41

Sensitivity of amylopectin nitrate loaded at a density of 1.0 gm./cc. to initiation by lead azide

Wt. in mgm. of Lead azide	Weight of sand in grams pulverized finer than 0.590 mm. by *reenforced electric detonator* containing 0.6 gm. of 13.25% N amylopectin nitrate					
	First trial	Second trial	Third trial	Fourth trial	Fifth trial	Mean
20	1.05	1.20				1.13
22	0.95	1.10				1.03
24	1.30	1.35				1.33
26	69.25	70.95	71.40	70.60	66.15	69.67
28	69.20	72.90	71.35	70.45	67.50	70.28
30	70.15	70.30	68.80	69.70	72.55	70.30
32	71.15	73.05				72.10
34	72.00	73.30				72.65
36	72.05	74.10				73.08

Sensitivity of amylopectin nitrate to initiation by lead azide

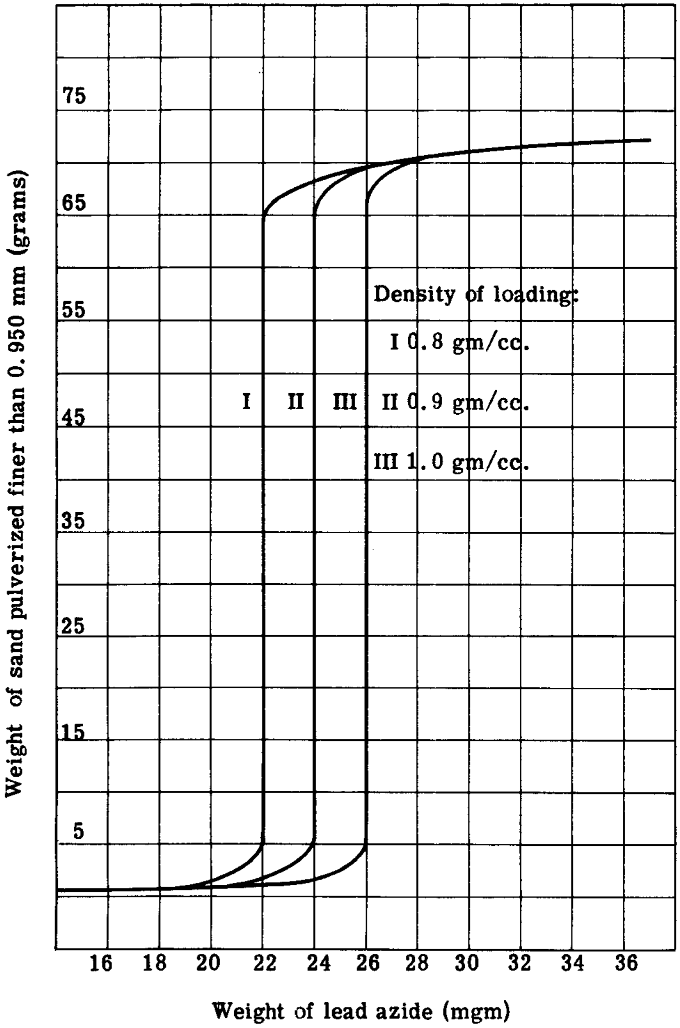


Figure 50

4. Performance characteristics (127)

The function of an explosive is to do useful work conveniently and efficiently, the amount of useful work being done outlines its performance characteristics. Thus, in connection with the relative safety evaluation, relative performance should also be considered.

4.1 Determination of power

The Trauzl test (128) measures the comparative diruptive power of explosives when fired under moderate confinement by the enlargement of a cavity in a plastic mass. In making the test, equal weights of different explosives are confined by means of a fixed quantity of stemming, into boreholes of definite dimensions, made in lead blocks of prescribed character, and then exploded by means of similar detonators. In this test every effort is made to have each factor alike, except the character of the explosives being compared. The measure of the test is the volume by which the cavity in the block is increased as a result of the pressure exerted by the explosive in exploding under the degree of confinement to which it is subjected. The degree of confinement depends on the quantity of stemming used and the firmness with which this stemming is tamped.

4.1.1 Description of blocks

The cylinderical lead blocks are cast in a mold being prepared from desilverized lead of the best quality. All castings are made under identical conditions and from the same lot of lead, so that variations resulting from differences in the casting procedure and material used are eliminated. Each block is 200 mm. in diameter and 200 mm. in height, and has a borehole 25 mm. in diameter and 125 mm. in depth which is centrally located in its upper surface.

The material used in stemming is sand containing only a trace of moisture and of such a texture that it passes through a 30-mesh screen but not through an 80-mesh screen. Fifty cubic centimeters of this sand is used in each test.

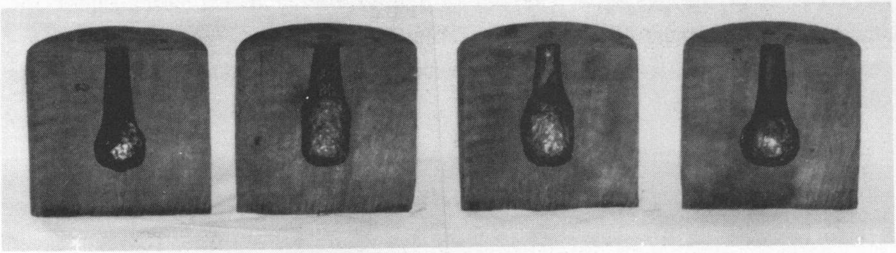
4.1.2 Test method

A piece of tin foil is cut in the shape of a trapezoid, with sides 150 and 130 mm. long and with a width of 70 mm. A 10 ± 0.01 gram sample of the explosive to be tested is then wrapped in the tin foil so as to make a cartridge 25 mm. in diameter.

A Nobel-Troisdorf "Briska" electirc detonator No. 8 is inserted into the center of the charge, and the charge then inserted in the bore hole. The latter is filled with the quartz sand without tamping, the temperature is recorded, and the charge then fired with a small generator twist type blasting machine. The hole is cleaned from adhering matter and its volume to the nearest cubic centimeter is measured by filling it with water from a burette. The increase in volume is computed to the nearest cubic centimeter.

4.1.3 Test results

Figure 51 illustrates four cross-sections of lead blocks showing the enlargements caused by TNT, Amylose nitrate, Amylopectin nitrate, and Hexogen.



TNT Amylose nitrate Amylopectin nitrate Hexogen

Figure 51
Cross-sections in lead blocks

The results of comparative tests of TNT, Amylose nitrate 13.37% N, Amylopectin nitrate 13.25% N, and Hexogen are given in table 42. The low density of the starch nitrates necessitated the use of 5 gram charges.

Table 42

Explosive	Enlargement cc		
	First trial	Second trial	Mean
TNT	129	129	129
Amylose nitrate	184	169	176.5
Amylopectin nitrate	189	189	189
Hexogen	196	189	192.5
Temperature 16°C			

4.2 Determination of brisance

The Kast test (129) measures the comparative shattering power of explosives through the crushing effect of a metal cylinder. In making the test, the different explosives are loaded in zinc cartridges of definite dimensions and fired on a brisance meter with the aid of an electrical detonator. The measure of the test is the compression of a small copper cylinder caused by the pressure exerted on it as a result of the force of explosion.

4.2.1 Description of the brisance meter

The brisance meter illustrated in figure 52 consists of a hard steel base A, fitted with a hollow normal steel cylinder B, having two opposite round openings near its base to eliminate air compression. In this cylinder moves a hard steel piston C, weighing 623 grams, and which carries a strong nickel steel piston C, weighing 460 grams and secured in place by a brass ring E. This plate is protected above by three round discs, the inner one being of iron and the outer two of lead.

4.2.2 Test method

A zinc cartridge of 21 mm. internal diameter, 21.6 mm. external diameter, and 80 mm. in hight is filled with the explosive under test and the density of loading calculated. A small copper cylinder 7 mm. in diameter and 10.5 mm. in height is placed centrally between the base A and the piston C. The zinc cartridge is placed over the center of the upper protecting lead disc and secured in place. The explosive is detonated by means of a 25 gram Pentastit detonator initiated by a Nobel-Troisdorf "Briska" electric detonator No. 8. The temperature is recorded and the charge is fired with a small generator twist type blasting machine. The height of the copper cylinder is measured precisely and the compression is computed to the nearest hundredth of a millimeter.

4.2.3 Test results

The results of comparative tests of TNT, Amylose nitrate 13.37% N, Amylopectin nitrate 13.25% N, and Hexogen are given in table 43.

Table 43

Explosive	Density	Compression mm.	Compression %
Amylose nitrate	0.445 0.441	0.90 0.80	8.57 7.62
Amylopectin nitrate	0.429 0.446	0.92 0.90	8.76 8.57
Hexogen	0.657 0.635	1.78 1.81	16.95 17.24
TNT	0.664 0.700	1.32 1.94	12.57 18.48

Temperature 20°C

The comparative results of the already described sand test are given for TNT, Amylose nitrate 13.37% N, Amylopectin nitrate 13.25% N, and Hexogen in table 44.

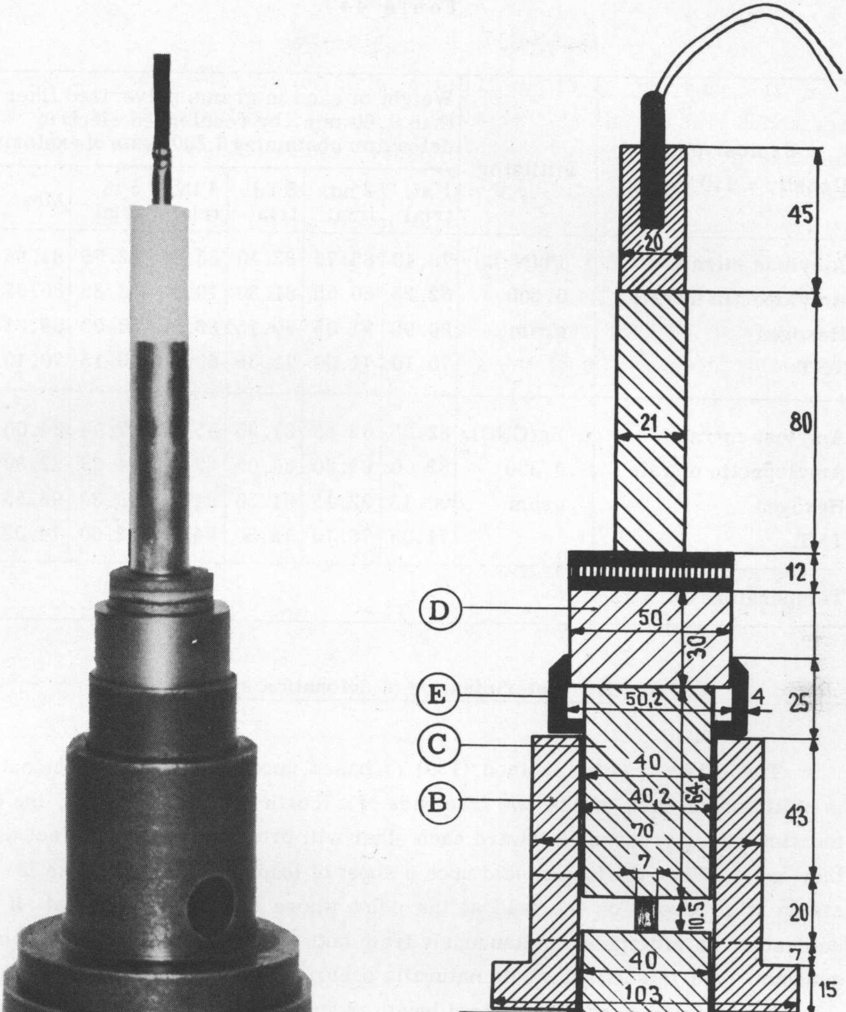


Fig. 52 Brisance meter
(Courtesy Schweiz. Sprengstoff-Fabrik AG. Dottikon)

Table 44

Explosive Density = 1.0 gm/cc.	Inititator	Weight of sand in grams pulverized finer than 0.60 mm. by reenforced electric detonator containing 0.600 gram of explosive					
		1 st. trial	2 nd. trial	3 rd. trial	4 th. trial	5 th. trial	Mean
Amylose nitrate	$Pb(N_3)_2$ 0.200 gram	78.10	85.75	83.10	80.05	82.75	81.95
Amylopectin nitrate		82.25	80.55	81.30	79.90	76.35	80.07
Hexogen		90.95	91.05	89.15	86.50	88.90	89.31
TNT		70.10	71.00	71.35	69.90	68.15	70.10
Amylose nitrate	$Hg(ONC)_2$ 0.300 gram	82.35	82.45	81.35	85.95	87.90	84.00
Amylopectin nitrate		82.00	84.80	80.05	82.65	84.55	82.80
Hexogen		90.15	92.15	91.50	94.90	98.30	93.55
TNT		71.05	76.10	75.50	74.85	72.60	74.02

Temperature 18.5°C

4.3 Determination of detonation speed

The D'Autriche method (130) is based upon the fact that if detonation is initiated in each of the two free ends of a length of detonating fuse, the detonation waves proceeding toward each other will produce a marked effect when they meet. When the fuse is laid upon a sheet of lead, a marked linelike incision is produced on the lead at the point where the two waves meet. If the detonation is initiated simultaneously from both ends, and if the fuse is homogeneous, then this effect would naturally occur at the exact middle of the fuse.

If one interposes a measured length of an explosive between the two ends of a length of detonating fuse and a detonation wave is initiated simultaneously at adjacent ends of explosive and fuse, the wave will be initiated at the other end of the fuse only after it passes over the entire length of explosive. Thus, the two detonation waves will meet beyond the median line of the fuse by a distance relative to the time taken by the wave to travel through the interposed explosive.

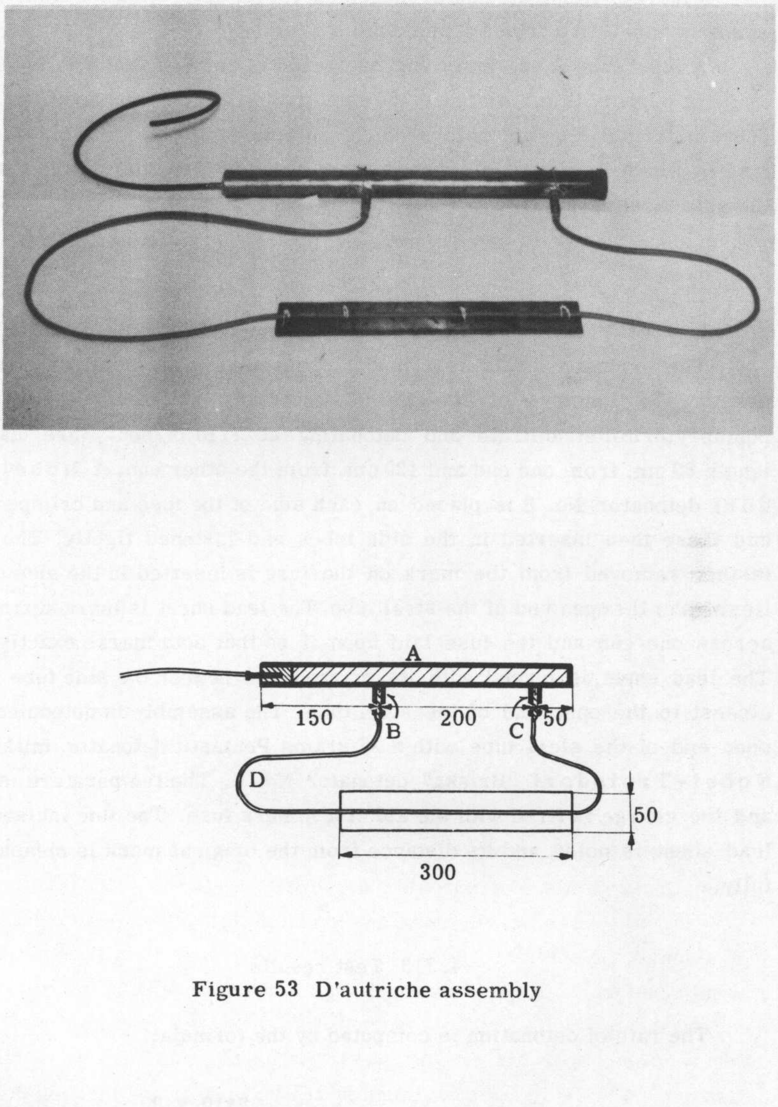


Figure 53 D'autriche assembly

4.3.1 Description of the test assembly

Figure 53 illustrates the arrangement for the determination of the detonation speed by the D'Autriche method.

A steel tube A 400 mm. long, is opened at one end, and has two side tubes made of copper, B at a distance 150 mm. from the open end and C at a distance 200 mm. from B. Two detonators which are crimped to the ends of the detonating fuse D, which in turn is laid upon a sheet of lead 3 mm. thick, are inserted into the side tubes B and C.

4.3.2 Test method

The explosive under test is compressed into the steel tube to a known density. Two meters of Nobel-Troisdorf detonating fuse, containing pentaerythritoltetranitrate and detonating at 7110 m/sec., are marked at a length 80 cm. from one end and 120 cm. from the other end. A Nobel-Troisdorf detonator No. 8 is placed on each side of the fuse and crimped in place, and these then inserted in the side tubes and fastened tightly. The detonator farther removed from the mark on the fuse is inserted in the side tube which lies nearer the open end of the steel tube. The lead sheet is marked transversely across one end and the fuse laid upon it so that both marks exactly coinside. The lead sheet is placed with its marked end nearer the side tube which lies closest to the open end of the steel tube. The assembly is detonated from the open end of the steel tube with a 25 grams Pentastit detonator initiated by a Nobel-Troisdorf "Briska" detonator No. 8. The temperature is recorded and the charge is fired with the aid of a miners fuse. The line incised upon the lead sheet is noted and its distance from the original mark is measured carefully.

4.3.3 Test results

The rate of detonation is computed by the formula:

$$\text{Rate of detonation} = \frac{7110 \times 20}{2\,(20 + \text{Distance on lead sheet between the marks})}$$

The results of the detonation speed of Amylose nitrate 13.37% N, and Amylopectin nitrate 13.25% N in tubes of various diameters are given in table 45.

Table 45

Explosive	Amylose nitrate	Amylopectin nitrate
Tube diameter mm.	25/35	25/35
Density gm/cc.	0.384	0.402
Speed of detonation m/sec.	2185	3175
Tube diameter mm.	30/33	30/38
Density gm/cc.	0.377	0.372
Speed of detonation m/sec.	3340	2755
Temperature 16°C		

4.4 Discussion of the performance results

The main conclusions which can be drawn from comparing the data of performance characteristics may be summerized as follows:

1. The power of amylose and amylopectin nitrates is of the same order as that of Hexogen and about 1.4 times that of TNT.

2. The brisance of Hexogen, amylose nitrate, amylopectin nitrate, and TNT when loaded at the same density decreases in the order named.

3. These conclusions are in harmony of the theoretical considerations layed down by Lothrop and Handrick (131) regarding the relationships existing between the performance of explosives and their constitution. These authors showed that power as measured in the Trauzl lead block, and brisance are at a maximum for carbon and hydrogen compounds which bear only nitrate ester, nitramine, or nitro groups as substituents, and are at or close to zero oxygen balance. The power and brisance are directly related to oxygen balance having maximum values when the balance is zero. When the oxygen balance either increases or decreases from zero the power and brisance gradually decrease.

TNT, amylopectin nitrate (13.25% N), amylose nitrate (13.37% N), and Hexogen which have the oxygen balance values -74.0, -31.5, -31.0, and -21.6, produced enlargements in the lead block cavity amounting to 129, 176.5, 189, and 192.5 cubic centimeters, respectively. In the sand test, when loaded at a density of 1.00 gm/cc., they crushed 74.00, 82.80, 84.00, and 93.50 gram of sand respectively.

4. The data on brisance by compression of copper cylinder and speed of detonation is limited to low loading densities. It is not possible to interpret such data since the density of loading is not constant.

SUMMARY

Part I
STARCH

1. A summary of the composition and properties of starch is given, with a brief description of the fractionation techniques employed for separating starch into amylose and amylopectin.

2. Hot water fractionation of Egyptian rice starch at 80°C gives about 64% amylopectin and 28% amylose.

Part II
NITRATION OF STARCH

3. A comprehensive historical survey of starch nitration is given, with a detailed description of the du Pont nitrometer and the mathematical relationships accompanying the nitration process.

4. A detailed study on the nitration of amylose with nitric acid-acetic anhydride mixtures is undertaken to evaluate the optimum conditions for nitration. The study established the following facts:

(a) The activity of Orton's mixture shows an optimum when the nitric acid is in slight excess of the stoiciometric ratio of acetyl nitrate formation. This falls in the region where the mixture contains equal volumes of nitric acid and acetic anhydride.

(b) When the ratio of the components of Orton's mixture is changed, the degree of nitration of amylose decreases.

(c) This optimum composition has a marked swelling effect on the amylose accompanied by a sudden evolution of heat, and produces an increase in viscosity, dependent on the amount of amylose present.

(d) With a rise in temperature, the degree of nitration is slightly increased; the increase being very marked in the region of optimum composition.

(e) The degree of nitration increases with time till an equilibrium is reached, after which the nitrogen content of the product steadily decreases.

5. The above effects are interpreted by assuming that the nitration proceeds by the way of dinitrogen pentoxide formed in the following system of reactions:

$$HNO_3 + Ac_2O \rightleftharpoons AcOH + AcONO_2 \qquad (1)$$
$$2\ AcONO_2 \rightleftharpoons Ac_2O + N_2O_5 \qquad (2)$$
$$AcONO_2 + 3\ HONO_2 \longrightarrow C(NO_2)_4 + 3\ H_2O + CO_2 \qquad (3)$$

Thus, excess acetic anhydride will shift equation (2) to the left and destroy the effective nitrating entity, dinitrogen pentoxide. Moreover, excess nitric acid favours the secondary oxidation reaction (3), thus, destroying acetyl nitrate and again shifting equation (2) to the left. Besides, the swelling effect of the medium containing equimolecular quantities of anhydride and acid promotes reactivity only because the presence of large solvating groups allows channels to be formed large enough to allow dinitrogen pentoxide to penetrate the structure.

To account for the increasing degree of nitration with a rise in temperature, it is assumed that the equation (2) is catalyzed by increasing temperature. After the estrification reaction reaches certain point, the phenomenon of denitration supervenes. Secondary reactions play a role in diluting the spent acid, thus, favouring ester hydrolysis.

6. A detailed study of the nitration of amylopectin with nitric acid in the presence of pyridine is also undertaken to evaluate the effect of nitration parameters of such a homogeneous single phase nitration. The study established the following facts:

(a) The activity of the medium is enhanced by an increase in the quantity of nitric acid added.

(b) The nitration is extremely fast and the estrification equilibrium is reached at a relatively low degree of nitration, then denitration supervenes.

(c) The degree of nitration is favoured by an increase of temperature and a decrease of amylopectin concentration.

7. The above effects are interpreted from the fact that in the presence of pyridine, nitric acid will be deprotenized, furnishing nitrate ions which anticatalyze nitronium ion formation from nitric acid. Mediums containing low nitric acid concentrations are relatively inactive and result in slowness and incompletness of the reaction. Thus, it is necessary to maintain a high concentration of nitric acid. The increasing degree of nitration with increasing temperature is attributed to an increase in the nitrating entities derived from nitric acid by shifting the equilibria in a favorable direction.

Part III

STABILIZATION OF STARCH NITRATES

8. A comprehensive historical survey of the stability properties and the stabilization treatments of starch nitrates is given, with a detailed description of the stability tests concerned.

9. A detailed study on the stability of the material nitrated by Orton's mixture is conducted by repeatedly boiling the product in acidic and alkaline mediums. The main conclusions to be derived from the study are:

(a) By repeatedly boiling the product in water in either an acidic or an alkaline medium a decrease in the nitrogen content is observed. This is apparently due to the hydrolysis of the nitrate groups and the subsequent liberation of nitric acid. The volatility of tetranitromethane which is present as an impurity also plays a role in diminishing the nitrogen content.

(b) Repeated boiling with water in either an acidic or an alkaline medium causes a gradual increase in the stability of the product as judged by increasing ignition points, increasing Abel periods, and increasing Bergmann-Junk values. Boiling washes out any free mineral acid and nullifies its detrimental effect on stability; besides, the highly unstable tetranitromethane is driven off because of its volatility.

(c) Higher denitration and higher stability are attained in alkaline rather than acidic mediums. This is attributed to two reasons. In the first place, alkaline hydrolysis is more rapid and more effective than acid hydrolysis; and secondly, tetranitromethane acts as a powerful oxidizing agent and produces unstable nitrated oxidation products, which are more easily decomposed in dilute alkaline rather than dilute acid mediums.

(d) Amylose nitrate is more stable than whole starch nitrate, while amylopectin nitrate is less stable. Amylose nitrate, like the parent substance amylose, possesses a simple regular crystalline micellar structure, and impurities are so entangled that their rate of diffusion out of the structure will be very slow. Due to this structural difference, amylose nitrate is inherently more stable than amylopectin nitrate; and the parent substance, starch nitrate, thus possesses a medium stability.

(e) In nitric acid-acetic anhydride nitration, the stability of the product is greatly improved after a short period of boiling, as compared with mixed acid nitration. In mixed acid nitration the instability is due to the formation of sulphonic acid esters which are difficult to hydrolyze. However, nitration by Orton's mixture introduces only tetranitromethane, an impurity which is easily removed with steam.

10. Alcohol fractionation of nitrated starch, amylose, and amylopectin produces increased stability in both the soluble and insoluble fractions, the latter fraction being always the more stable. One explanation for this stabilizing action is that fractionation removes traces of tetranitromethane which is known to be soluble in alcohol.

Part IV

EXPLOSIVE PROPERTIES OF STARCH NITRATES

11. A comprehensive historical survey of the explosive properties and applications of nitrostarch and compostions containing it is given, including a detailed description of the sensitivity and performance tests concerned.

12. The study of the sensitivity of amylose and amylopectin nitrates to direct impact, frictional impact, and detonation by initiators shows that:

(a) The maximum impact energy for zero probability of detonation is 0.4 kg.m. for amylose and amylopectin nitrates, 1.4 kg.m. for TNT, and lower than 0.4 kg.m. for Hexogen.

(b) Amylose and amylopectin nitrates, TNT, Hexogen, and PETN show dead sensitivity to explosion by frictional impact stimulus.

(c) Amylose nitrate when loaded at the densities 0.8, 0.9, and 1.0 can be detonated completely by 220, 230, and 240 milligrams of pure mercury fulminate, respectively.

(d) Amylopectin nitrate when loaded at the densities 0.8, 0.9, and 1.0 can be detonated completely by 22, 24, and 26 milligrams of pure lead azide, respectively.

13. The comparative study of amylose and amylopectin nitrates, TNT, and Hexogen with respect to their performance characteristics shows that:

(a) The power of amylose and amylopectin nitrates is of the same order as that of Hexogen and about 1.4 times TNT.

(b) The brisance of Hexogen, amylose nitrate, amylopectin nitrate, and TNT when loaded at the same density decreases in the order named.

ZUSAMMENFASSUNG

Der 1. Teil der Arbeit gibt eine Zusammenstellung der Literatur über die Zusammensetzung und die Eigenschaften der Stärke in Amylose und Amylopektin angewendeten Methoden. Die Heisswasser-Fraktionierung von aegyptischer Reisstärke liefert 64% Amylopektin und 28% Amylose.

Der 2. Teil der Arbeit behandelt die Nitrierung von Stärke. Nach einer Uebersicht über die bisherigen Arbeiten wird eine detaillierte Beschreibung des Dupont'schen Nitrometers und die mathematischen Beziehungen des Stärkenitrierungsprozesses gegeben. Die Veresterung von Amylose mit Salpetersäure in Essigsäureanhydrid wurde eingehend studiert, um die optimalen Versuchsbedingungen zu ermitteln. Sie liegen bei einem nahezu stöchiometrischen Verhältnis von Essigsäureanhydrid und Salpetersäure. Abweichungen von den optimalen Verhältnissen führen zu Produkten mit geringem Stickstoffgehalt. Das optimal zusammengesetzte Gemisch aus Salpetersäure und Essigsäureanhydrid bewirkt eine starke Quellung der Amylose unter Erwärmung und Viskositätserhöhung. Temperaturerhöhung gibt nur eine geringe Erhöhung des Stickstoffgehaltes, der bei dem optimalen Verhältnis wesentlich deutlicher wird.

Der Veresterungsgrad nimmt mit der Zeit bis zu einem Gleichgewicht zu. Bei weiterer Behandlung nimmt der Stickstoffgehalt wieder stetig ab. Für die Erklärung dieser Erscheinung wird angenommen, dass Stickstoff-Pentoxyd das wirksame Agens der Reaktion darstellt, insofern als es mit Essigsäureanhydrid unter Bildung von Acetylnitrat reagiert. Ein Ueberschuss von Salpetersäure führt zur Bildung von Tetranitromethan unter Zerstörung des Acetylnitrats.

Eine eingehende Untersuchung der Nitrierung von Amylopektin mit Salpetersäure in Gegenwart von Pyridin ergab eine homogene Phase mit starker Reaktionsbeschleunigung, doch liegt das Veresterungs-Gleichgewicht bei einem niedrigen Veresterungsgrad. Temperaturerhöhung und Verminderung der Amylopektin-Konzentration bedingen eine Erhöhung des Veresterungsgrades. Es wird angenommen, dass das Pyridin die Bildung von Nitronium-Ionen aus Salpetersäure hemmt. Niedrige Salpetersäure-Konzentrationen sind in Gegenwart von Pyridin verhältnismässig inaktiv; sie vermindern die Reaktionsgeschwindigkeit und geben unvollständige Veresterungen. Höhere Temperaturen begünstigen die Veresterung in Gegenwart von Pyridin.

Der 3. Teil der Arbeit behandelt die Stabilisierung der Nitrostärke und die bisher bekannten Methoden zur Bestimmung des Stabilisierungsgrades. Die Stabilisierung wurde in saurem und alkalischem Medium näher untersucht. Die Säure- und Alkalibehandlung führt zu einer Verminderung des Stickstoffgehaltes unter teilweiser Verseifung und Bildung von Tetranitromethan. Als beste Stabilisierungsmethode wurde Kochen mit sehr verdünnter Ammoniaklösung erkannt. Dabei wird das sehr instabile Tetranitromethan entfernt und andere instabile Verunreinigungen des Stärkenitrates zerstört. Die alkalische Stabilisierung ist der sauren überlegen.

Amylosenitrat ist viel stabiler als Amylopektinnitrat und das Nitrat von natürlicher Stärke. Die Ursache dafür wird in der kristallinen Struktur der Amylose gesehen. Die verzweigten Moleküle des Amylopektinnitrates erschweren die Entfernung der Verunreinigungen. Kurze Behandlung in Essigsäureanhydrid-Salpetersäure erhöht die Stabilität beträchtlich. Gegenüber der Nitrierung von Stärke mit Nitriersäure hat die Veresterung von Stärke mit Essigsäureanhydrid-Salpetersäure den Vorteil, dass keine Schwefelsäureester gebildet werden und das leicht entfernbare flüchtige Tetranitromethan als Nebenprodukt entsteht.

Durch Fraktionierung von Stärkenitrat, Amylosenitrat und Amylopektinnitrat aus alkoholischer Lösung erhält man stabilere Produkte, indem auch hier das Tetranitromethan entfernt wird.

Der 4. Teil der Arbeit behandelt die explosiven Eigenschaften der Stärkenitrate. Nach einem Ueberblick über die Literatur wird über die eigenen Versuche berichtet. Dabei hat sich folgendes ergeben: Die Schlagempfindlichkeit von Amylose- und Amylopektinnitrat ist etwas besser als bei Hexogen, aber geringer als bei Trinitrotoluol. Die Reib- und Detonationsempfindlichkeit genügt den praktischen Anforderungen. Die Explosionswirkung von Amylose- und Amylopektinnitraten ist gleich wie bei Hexogen und deutlich höher als bei Trinitrotoluol. Die Brisanz der Stärkenitrate liegt zwischen Hexogen und Trinitrotoluol.

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Curriculum vitae

I was born on November 3rd 1925 in Alexandria, where I completed my primary education in 1938 and my secondary education in 1944. I joined The Institute of Chemical Technology of Alexandria University and graduated in 1948 with the degree of B.Sc.Tech.(Hons.). In the same year I was appointed as a demonstrator at The Institute of Chemical Technology of Alexandria University, where I carried out research work under the supervision of Prof. Dr. Karl Lauer, late director of the Institute, and obtained the degree of M.Sc.Tech.in 1952. Beside my work as a demonstrator, I was authorized to work as the Institute's Librarian.

In July 1953, I joined The Swiss Federal Institute of Technology on a mission from the Egyptian Government to study for a doctorate in Explosives Technology under the supervision of Prof. Dr. Heinrich Hopff.

Zurich, September 1955. Zakaria Shalash