WAR RESEARCH

A. A Nitroguanidine-Formaldehyde Explosive Polymer of Resin Type

B. Crystal Size-Reduction of Nitroguanidine by Acidic Formaldehyde Solution

A Thesis

by

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By this process the crystal size and specific surface are controlled by varying the formaldehyde concentration. Thus, from solutions containing 0.3% to 1.3% formaldehyde there is a continuous decrease in crystal size and increase in specific surface from 2 x 25 microns and 28,000 cm^2/cm^3 to less than 1 x 4-8 microns and 70,700 cm^2/cm^3 respectively.

The problem may be divided according to the following uses:

(a) A product which can be employed as a phlegmatizer for high explosives.

(b) A product which can be used as a binder in burning mixtures.

(c) A product which can be used to give crystalline high explosives a fluidity suitable for shell-pouring and which sets to form a rigid mass.

HISTORICAL INTRODUCTION

The roots of the chemistry of high polymers go back to the middle of the last century. Organic chemists have come across high polymeric substances innumerable times in the course of their studies on low molecular compounds. However, since high polymers do not crystallize and are difficult to characterize they were justly regarded as unsuitable objects of research and were not extensively examined. During the past decade however, the number of papers on the deliberate preparation of high polymers has increased particularly, and at present, as is shown by a survey of the literature, a large number of papers on the subject of polyreactions is published annually. While our knowledge of the synthesis of polymers was gradually increasing during the last twenty years, there was one natural product which particularly aroused the interest of the chemists, namely: cellulose. The combined efforts of organic chemists the world over have finally succeeded in establishing a satisfactory structural principle which is successfully applied to other natural and synthetic high polymers. All experimental facts point in the direction that the high polymers, natural and synthetic, consist of large molecules which contain several hundreds and thousands of atoms bound together by normal homopolar covalences.

The literature on high polymers is widely scattered and extends largely into technical and patent publications. Due to the

commercial nature of the products of polyreactions, particularly polycondensation reactions, the present situation is such that, though the number of publications is extremely large, their purpose is mainly to determine and explore the conditions under which products of definite and desired properties can be made. They show less interest in speculations regarding the mechanism of the reactions. However, the interest of industry is increasing rapidly along with a desire to understand these reactions which are responsible for many excellent and valuable synthetic products of modern technology.

The Nature of Polymer Formation

In addition to cellulose, rubber, proteins, and certain other natural products, the organic high polymers include substances which may be synthesized. The initial substances must consist of molecules of rather low molecular weight which are capable of uniting with at least two other molecules. Such substances are described by Carothers (1) as bi-functional. The transformation of various low molecular weight compounds into complex derivatives is usually termed polymerization, but in polymerization two very distinct types of reaction can be distinguished. Many bi-functional molecules are capable of reacting without undergoing any change in percentage composition, and the reactants are marked by a large degree of unsaturation; in this case we speak of addition polymerization. In others, combination is accompanied by the elimination of simple compounds such as water. This type of

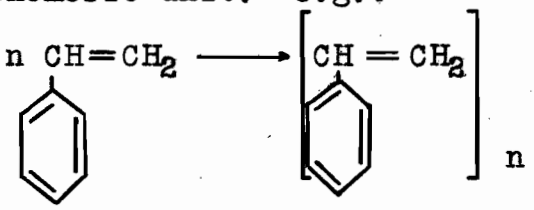
polymerization is known as condensation polymerization.

Classification of Addition and Condensation Polymerization.

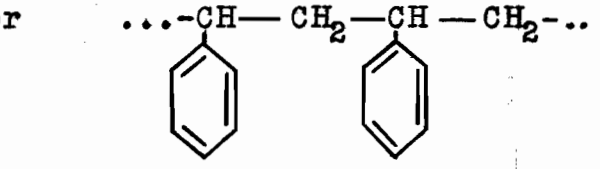
A. Addition Polymerization:- Homo-polymerization is a species in which the polymer is built up by additive combination of like monomer groupings. The process may be shown schematically as:

$$nA \longrightarrow (A)_n \quad \text{or} \quad \cdots\cdots\text{-A-A-A-A-}\cdots\cdots$$

where n represents the number of monomeric groups and A the monomeric unit. e.g.:



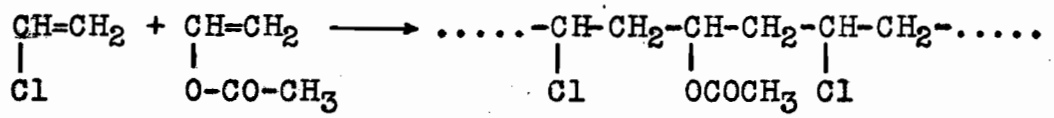
or



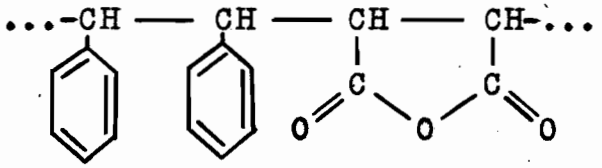
Co-polymerization is the term applied when two or more substances polymerize at the same time. The process may be shown schematically as:

$$n\,B + n\,C \longrightarrow (BC)_n \quad \text{or} \quad \cdots\cdots\text{-B-C-B-C-B-C-}\cdots\cdots$$

eg:



Hetero-polymerization is a special case of co-polymerization which involves the combination of a polymerizable i.e. an unsaturated substance and another unsaturated substance which by itself does not readily polymerize. Though maleic anhydride does not ordinarily polymerize, it will combine with stilbene in boiling xylene (2) The structure has been represented as



The kinetics of polymerization of the additive type are clearly given in K.H. Meyers' discussion of synthetic high polymers in "High Polymers", Vol. IV, p. 93, (1942), Interscience Publishers, New York, N.Y.

Broadly speaking, any unsaturated grouping, such as the acetylenic-, ethylenic-, nitrile-, imino- or carbonyl-group, acts as a polymerizing factor. The capacity for polymerization is determined however, not only by the grouping itself, but also by external factors such as heat, light, pressure and catalysts. With regard to the catalysts, there are two distinct groups. They are: (a) those such as oxygen and peroxides that give free radicals, and (b) those such as acids that function through an ionic mechanism.

If all the unsaturation is on a single atom,

$$\rangle C=C=C\langle \quad , \qquad \rangle C=C=O \quad , \qquad \rangle C=C=N- \quad , \qquad -N=C=N-$$

the tendency for polymerization is greater. Conjugation of the groupings is even more effective.

$$\rangle C=C-C=C\langle \quad , \qquad \rangle C=C-C=O \quad , \qquad \rangle C=C-C=N-$$

$$O=C-C=O \quad , \qquad -N=C-C=N-$$

Additional conjugation further increases the tendency toward polymerization.

$$\rangle C=C-C=C-C=C\langle \quad , \qquad \rangle C=C-C=C-C=O \quad , \qquad \rangle C=C-C-C=C\langle \quad (O \text{ on } C)$$

B. Condensation Polymerization:- This type takes a variety of forms in the same manner as the additive type. Single condensations do not yield a polymeric substance. In order to build up a large molecule, the reacting molecule must have more than one grouping to allow a multicondensation to take place.

$$D_x + D_x \longrightarrow D\text{-}y\text{-}D\cdot + z$$

e.g.: $CH_3COOH + CH_3COOH \longrightarrow CH_3CO\text{-}O\text{-}CO\text{-}CH_3 + H_2O$

In this instance, a condensation has taken place, but no polymer results. With two reacting groups, or as they are more usually termed, functional groups, several reactions may take place.

(a) Intramolecular condensation:

$$x\ D_x \longrightarrow \boxed{D\text{-}y} + z$$

e.g.: $HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH \longrightarrow \underbrace{CO\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}O} + H_2O$

(b) The reaction may be intermolecular to build up a long chain and then become intramolecular:

$$x\text{-}D\text{-}x \longrightarrow x(D\text{-}y\text{-}D\text{-}y\text{-}D\text{-}y)_n\text{-}x \longrightarrow \boxed{(D\text{-}y)_m}$$

(c) The reaction may be wholly intermolecular and yield a linear polymer:

$$x\text{-}D\text{-}x \longrightarrow x\text{-}D\text{-}y\text{-}(D\text{-}y)_n\text{-}D\text{-}x$$

Analogous types of multicondensation to homo- and co-polymerization of additive type may be expressed as follows:

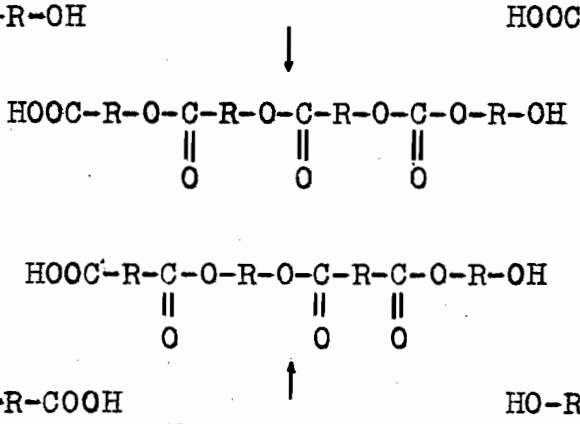
$$x\text{-}D\text{-}y \longrightarrow x\text{-}D\text{-}z\text{-}D\text{-}z\text{-}D\text{-}z\text{-}D\text{-}y$$

and $$x\text{-}E\text{-}x + y\text{-}F\text{-}y \longrightarrow x\text{-}E\text{-}z\text{-}F\text{-}z\text{-}E\text{-}z\text{-}F\text{-}y$$

An example of the different types of condensation can be seen in the formation of polyesters. The hydroxyl- and carboxyl-groups may exist in the same molecule and lead to a homo-condensa-

tion or the hydroxyl-groups may exist in one molecule and the carboxyl-groups in another. In both instances, esters will be formed but they will differ in arrangement.

eg.: HOOC-R-OH HOOC-R-OH

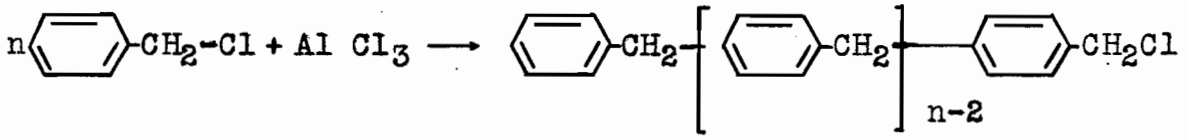


Numerous other types of condensation polymerization exist. For example, long chain paraffins can be built up by the action of sodium on the polyethylene bromides, followed by reduction in order to replace the terminal halogens by hydrogen (3).

$$Br\text{-}(CH_2)_{10}\text{-}Br + 2\ Na + Br\text{-}(CH_2)_{10}\text{-}Br \longrightarrow$$

$$Br\text{-}(CH_2)_{10}\text{-}\left[(CH_2)_{10}\right]_x\text{-}(CH_2)_{10}\text{-}Br \xrightarrow{red.} H(CH_2)_y\text{-}H$$

A bi-functional Friedel and Crafts reaction (4) leading to the formation of a polymerized material, can be seen in the action of aluminum chloride on benzyl chloride:

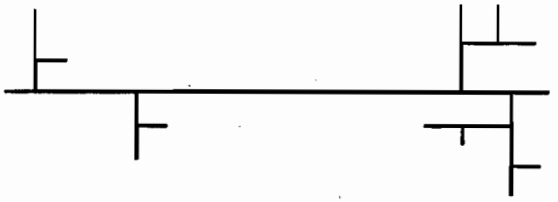


Two and Three Dimensional Polymers

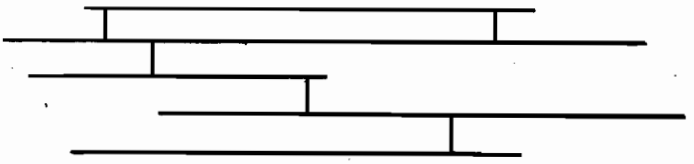
It is evident that bi-functional molecules can unite only to form chain molecules (linear polymers). If on the other hand,

the molecules are able to react with more than two molecules, (tri-, tetra- and poly-functional molecules) the polymerizing molecule is capable of linkage and growth in more than one dimension.

Chain branching may occur. This refers to a long chain molecule which is not straight but has several branches as shown:



Polymeric networks may be formed by cross-linking. In this case straight or branched chains with more than one main valence bridge are formed as shown:



In the case of chain branching, the single molecule still remains isolated from all surrounding molecules as far as chemical covalent bonds are concerned. A cross-linked polymer may in some cases be regarded as a single molecule, since, as a result of cross-linking, isolated chain molecules are no longer present. The product is no longer an assemblage of long molecular threads which may be separated by solvents or caused to slip over each other by mechanical deformation.

Linkage may also be brought about after polymerization by means of a reaction independent of the polymerization process. Included in this category of cross-linked materials which harden on curing (or heating) are phenolic- and urea-formaldehyde plastics or resins.

The following properties may be regarded as generally characteristic for chain molecules (5):

(a) An unlimited faculty for swelling and gradual formation of homogeneous solutions in suitable liquids.

(b) A more or less definite softening-zone below which the material possesses the properties of an amorphous solid, while above this region it may be considered to be a viscous liquid. The existence of a reproducible softening-zone is of great technical importance in the use of linear polymers, because in the case of plastics it permits the application of the extrusion method.

(c) Dilute solutions of linear polymers display all the properties of a molecularly dispersed system.

(d) Chain polymers are capable of reactions in the swollen state. They can undergo esterification, chlorination and various other reactions without appreciably changing the structure of the polymer.

The most significant features of cross-linked molecules are the following:

(a) A limited capacity to swell in a few solvents and the material never goes into solution.

(b) There is no definite softening-zone; they start to soften only at high temperatures with slow decomposition.

(c) They usually exhibit a greater resistance to abrasion, impact and heat than linear polymers.

(d) With increasing cross-linking the possibility of reactions decreases and eventually disappears completely.

Structure of Polymers

The interest in such substances as resins, rubbers and fibrous materials such as cellulose has brought divergent views concerning their structure. These compounds can be represented very simply by the empirical formulas:

$(C_8H_8)_n$ - polystyrene
$(C_5H_8)_n$ - rubber (polyprene)
$(C_6H_{10}O_5)_n$ - cellulose

where n indicates not only an unknown magnitude, but also an unknown quality or kind of aggregation by which the units are united.

At least three different concepts have been utilized in an attempt to explain the manner in which these basal or structural units are bound. The first, with which Staudinger's name is associated (6), is that the structural units are bound together by primary (homopolar) valences. Opposed to this theory are those of Hess and Pringsheim (7), and of Bergmann (8). They are known as the association and the co-ordination theories respectively. Hess and Pringsheim believe that the unit

structures are monomeric or dimeric and are held together by secondary valence forces or by association. Bergmann's theory is that the structural unit is co-ordinated in the solid state and the unit, as such is incapable of free existence in solution. The structural units are associated in the large molecules by supermolecular affinities similar to that of molecules in a crystal lattice and, as in the crystal, the unit loses its independence and individuality as such within the larger aggregate.

Following the establishment, by X-ray analysis of definite periodicity in rubber, cellulose (9) and polyoxymethylene, (10) Mark and Meyer (11) proposed their 'micellar' theory where the high molecular weight organic compounds are considered to be linked together into chains by primary valence forces. Bundles of these chains are associated laterally by secondary valences to form micelles which act as entities and are responsible for the colloidal properties.

The primary valence theory is very useful in predicting properties. According to Staudinger, the molecules are thread-like chains of the monomeric groups linked together by primary valence bonds. As the degree of polymerization becomes greater, the molecular weight increases and the length of the chain likewise increases. The chain is in effect a single molecule and the properties of the polymer depend on the length. When the length of the chain is relatively short, hemicolloids are obtained. Longer chains lead to eucolloidal properties.

In hemicolloids, the mean molecular weight varies from 2,000-10,000 and the single molecule consists of approximately 50-100 monomeric units. Solutions of hemicolloids show relatively low viscosity and after the solution has been heated, the viscosity is not altered. The thermal softening-point is relatively low and the substance tends to be precipitated as an amorphous powder from solution upon the addition of a non-solvent.

Eucolloids (12) consist of molecules which are much longer than those of hemicolloids. The mean molecular weight varies from 10,000 to well above 100,000 and the chain may consist of as many as 3,000 monomeric units. The thermal softening-point of a eucolloid is high and the substance, in contrast to hemicolloids, is precipitated from solution as a material of a more or less fibrous nature. In solution, eucolloids have a high viscosity--a property which may be lowered by heat treatment. At the higher temperature, the longer chains are unstable and decompose into shorter ones.

Homologous Polymeric Series and Mixtures of Polymeric Homologues

From compounds of low molecular weight to high polymers there is a continuous transition through compounds of medium size. Lourenco (13) demonstrated this as early as 1863 and showed that the boiling-point and viscosity increased with increasing molecular weight. He obtained a series of polyethers

from the polymerization of ethylene oxide. Such a series is now described as a homologous polymeric series. Curtius (14) also showed a regular change in the various physical properties with molecular weight in homologous polymeric series.

At the present time a large number of homologous polymeric series is known. In the preparation of synthetic high polymers it is possible, according to the conditions, to obtain products of medium, high, or very high molecular weight. In fact the preparations obtained from natural products as well as those made by polyreactions are never uniform i.e., they are a mixture of homologous polymers.

The preparation of chemically pure substances (that is, substances composed of exactly identical molecules) from such mixtures of large chain molecules is not yet possible in the present state of technique (15). The purification of preparations is limited to obtaining mixtures of molecules of similar chain length by fractionation.

Since, in general, chemically pure preparations are not dealt with in this field, the idea of chemical purity should not enter into the formulation of concepts, into the statement of problems for solution or into the experimental treatment.

The Molecule and Molecular Weight

The term molecule denoted originally the group of atoms which persisted as a group in the gaseous state or in solution,

and whose size could be determined in these states by the usual methods adopted for the determination of molecular weight. However, the opinion (16) that high molecular substances are always present as free macromolecules is not supported by experiment and is too narrow a viewpoint for the explanation of the great number of facts in this field. Association by means of residual valences plays an important role in the chemistry of high polymers; here, the value of the molecular weight obtained from osmotic data represents not always the weight of the chemical molecule, but that of the group of associated molecules. On theoretical grounds one would expect the associated molecules to dissociate into chemical molecules at high dilution; but the required dilution is so high that in practice one is dealing with associated molecules.

Methods are available for the determination, by extrapolation, of the weight of particles present in solutions of most high polymers at infinite dilution, and hence for the determination of the chemical molecular weight. It is certain that only mean values are obtained since the preparations are mixtures. For the exact characterization of any particular preparation, it would be necessary to have data on the distribution of the molecules of different molecular weight about the mean molecular weight.

According to Meyer, the knowledge of the molecular weight of homologous polymeric mixtures is not of the same importance here as in the case of homogeneous substances. In general it

will suffice to have data indicating merely the order of the molecular weight, or one may even dispense completely with such figures, and use directly certain physical properties which depend on the molecular weight, for example, the viscosity or the solubility for the characterization of polymeric preparations.

Molecular Weight or Chain Length and Solubility.

By physical chemical considerations (17,18,19,20) it is shown that the solubility of a chain polymer is dependent on the length of the chains. If a precipitant such as a nonsolvent is added to a solution of a high polymer, when a certain concentration is reached, the homogeneous liquid separates into a mobile, liquid phase and a jelly. If a mixture of chains differing in length is present, it is possible by cautiously adding the precipitant, to produce a kind of fractionation in such a way that the most highly polymerized fraction is precipitated first, while the shorter chains remain in solution and are induced to flocculate only by the addition of more precipitant. In this way a solution of a high polymeric substance can be separated into fractions of similar chain length or molecular weight.

The Morphological Approach to the Chemistry of High Polymers

Since most natural high polymers occur in the solid state and since synthetic high polymers are used in the solid condition, it is necessary to pay more attention to this state of aggregation.

The mechanical properties are to a very large extent dependent on the type of aggregation or the texture, that is, the size, shape and arrangement of certain regularly built structural units, so that similar properties are encountered in substances differing in chemical constitution but similar in texture.

In the case of metals and silicates, the crystallites of which the sample is composed are often microscopically visible, so that the texture is relatively easy to investigate. In most organic high polymers, however, the largest regularly built structural units (mostly referred to as crystalline micelles) lie beyond the limit of resolution by the microscope.

In order to obtain as complete a picture of the whole structure as possible, it is desirable in the first place to investigate the spatial arrangement of the atoms within the molecules; next, the arrangement of the molecules to form micelles must be considered, and lastly, that of the micelles in the microscopic solid body.

The linear polymeric representations of synthetic materials have lent definite support to similar structures assigned to natural products. This has already been partly shown in the case of rubber. Other natural products which have been analogously treated are cellulose, wool, silk and other proteins. As evidence continues to accumulate, there appears to be a most intimate relation between resins, rubber-like products and fiber structures.

Much of the work which has been carried out on rubber and on fibrous structures is of immense importance in the field of synthetic resins. Rubber at low temperatures is hard and brittle and it may be that rubber has its chief virtue in the lucky circumstance of being elastic at room temperature. At high temperatures, rubber on treatment with air can be converted into a resin (21). On the other extreme, certain of the high-melting resins approach at high temperatures the rubber-like state; e.g. autopolymerized styrene behaves like raw rubber above 65°C. (22)

von Weirmarn (23) has called attention to the fact that linear polymers such as rubber, silk, resins, and lubricating oils may exist in mesomorphic state of matter.

von Weimarn (24) has succeeded in obtaining an unstable rubber-like substance from elementary sulphur. By pouring hot liquid sulphur at 400°C. in a thin stream into liquid air, solid and brittle threads are obtained; on warming, the threads acquire a high elasticity similar to that of rubber but the property disappears after a short time whereupon the sulphur becomes translucent and changes over to the normal viscous state.

Due to the rapid temperature drop of approximately 600°C., some of the molecules become orientated whereas others form a highly disperse glass. As the temperature rises, the glass melts into a viscous liquid, yielding a system with the highly elastic properties of rubber.

Just what exact relation exists between fibres, resins and rubber is at present hypothetical. Resins may be a mixture of

rod forms without any special attraction or repulsion in any one direction. In case of fibres these same rods might be arranged parallel with the attractive forces at the end of the rods, whereas in elastic substances there could be repulsive forces at the end of the chain so that they would attach themselves at right angles to one another. In such a stage any deformation would cause the substance to return to its undeformed condition (25).

Astbury and Woods (26) have deduced from X-ray investigation that fibres may exist in fully extended molecules in such compounds as cellulose, natural silk and stretched rubber. Folded or coiled molecules exist in unstretched rubber. The extended molecules lack elasticity, and fibres built up from such molecules extend through internal slippage.

Resins

A resin may be defined as a solid or semi-solid, complex, amorphous mixture of organic substances, having no definite melting-point and showing no tendency to crystallize. A resin is characterized by such physical properties as a typical luster and a conchoidal fracture rather than by any definite chemical composition (27).

The remainder of this discussion will consider only synthetic resins. A synthetic resin is simply a resin formed by synthesis using non-resinous materials as reactants.

Synthetic resins are often referred to as plastics, thus denoting that one of their uses is as a molding material. The term plastic is applied to anything which possesses plasticity,

that is, anything which can be deformed under mechanical stress without losing its coherence, and is able to keep the new form given it. It is obvious that materials which are plastic at ordinary temperatures will not form useful molded articles. Hence substances are used which are either thermoplastic or thermosetting.

A thermoplastic substance is one which is adequately rigid at normal temperatures and under ordinary conditions of stress, but is capable of deformation under heat and pressure. This property is permanent in a thermoplastic substance, that is, the process of deformation under these conditions can be repeated. In contrast to this is the term thermosetting. A thermosetting substance is one which possesses initially the properties of a thermoplastic but which under the influence of heat undergoes chemical change so that it is no longer thermoplastic but is permanently infusible. This type of plastic of course consists of the space polymers previously discussed (28).

The Resinous State

The nature of solids and liquids is perplexing and complicated save in idealized cases. Between the solid and the liquid there are a number of transitions which are of a puzzling character. A great number of names has been used to distinguish these intermediary states. They have been called gels, glasses, plastic, mesomorphic and amorphic states (29).

By considering matter as being divided into two classes, (30)

it is possible to avoid some of the ambiguity. In the crystalline state, matter is arranged in a definite order according to the laws of lattice structure. In the amorphous state, matter is in complete disorder.

Certain solid materials when dissolved in a volatile solvent and the solvent allowed to evaporate, instead of depositing as crystals, precipitate as an amorphous mass; or no solid separates but the solution becomes more viscous, yielding a solid as a vitreous- or glassy-mass. In the formation of crystals there is such a directing force between the molecules that at the point of crystallization the molecules become arranged in a lattice structure and solidification takes place rapidly. In the formation of amorphous materials, however, the attractive forces do not necessarily disappear, but no one force predominates and no regular lattice can be formed.

The formation of a glassy-mass can be observed not only when a solid is dissolved in a liquid, but also in the case of a pure substance. If a pure molten compound is cooled below its melting-point, the melt begins to crystallize at one or several points and at a few degrees below the melting-point, it is almost impossible to prevent the tendency to crystallization. If one quickly passes through this range of temperature, the tendency toward crystallization decreases and the melt may become viscous and solidify to a glass. In other words the rapid formation of the glassy-solid has prevented the atoms from arranging themselves in an orderly fashion. The general physical charac-

teristics of a glass are shown by many brittle synthetic resins, and according to Ellis, the lines of demarkation are exceedingly ill-defined. Tammann(31) performed various experiments that showed the structural similarity between resins and glasses.

Berger (32) considers the formation of a glass as a continuation process, taking place through a viscous supercooled state to the brittle state. Accordingly a break occurs in the property - temperature curve at the transition from the supercooled liquid. According to Tammannthis is displayed similarly in resins over a range of temperature. Brittle glass is, according to this concept, not merely a supercooled liquid, but represents a definite state of matter. According to a theory of the vitreous state developed by Rosenhain (33) glass is an assemblage of atoms in which certain molecular groupings may occur. Even in irregular assemblages of molecules, there are tendencies toward some aggregation even though most of the linkage bonds are unsatisfied.

Zachariasen (34) maintains that the atoms in glass are linked together by forces which are essentially that kind which exist in crystals. The mechanical properties of a glass are directly comparable to those of crystals, in fact, the strength of glass may excel that of the corresponding crystalline form. In glass, however, the atoms oscillate around definite equilibrium positions over large ranges of temperature and, even though one may consider a three dimensional network in glasses as in crystals, the network is not periodical and

symmetrical. The arrangement can not be entirely one of randomness, however, inasmuch as the internuclear distances do not sink below a given minimum value. The principal difference between the network in a crystal and that of glass is the symmetry and periodicity in the first instance and the absence of these properties in the latter. Each unit cell in a crystal must contain an integral number of stoichiometric molecules because all the unit cells are alike. In glass and resins, however, the unit cell is infinitely larger. As in crystals, the transparency of glasses and resins can be explained on the basis of an extended network.

Plasticity

Plasticity as well as viscosity both imply the meaning to flow, but it is generally conceded that soft solids do not behave in the same manner as viscous liquids. Because of overlapping of solids and liquids, differences in interpretation arise and no one definition can satisfactorily account for all of the conflicting phenomena. One of the most satisfactory definitions (35) is as follows: plasticity is the susceptibility to and the retention of deformation.

Part of the anomaly in plasticity can be avoided by the use of the classification of Polanyi, namely: that there are two forms of solid matter, crystalline and amorphous. In the ordered state are included metals and salts, whereas in the amorphous state are such substances as glass, varnishes and the like. These substances differ markedly with respect to plasticity. When amorphous materials change their form, the

molecules alter their positions. Increasing the temperature causes an increase in the mobility of the molecules. The plasticity of amorphous substances, therefore, is greatly dependent on temperature. In thermally plastic substances (glass, pitch, shellac, etc.) where plasticity depends on heat motion, one would expect that at absolute zero the plasticity would disappear (36). In crystalline substances, the plasticity even at high temperatures (i.e. below the melting-point) changes but very little due to the fact that the molecules are bound and cannot alter their positions (37).

The viscous layer between the particles, and the surface reaction i.e. the attraction between the liquid and the solvent phases is an important consideration since, substances which are wetted by a suitable liquid will form plastic masses (38). This type of plasticity has been termed "colloidal" because the most important factor appears to be the development of an active surface.

A phenomenon closely related to particle size and to loose packing is known as "thixotropy". A material is considered thixotropic when at rest it becomes solid but liquefies again on agitation. The phenomenon requires a sufficient thickness of liquid layers between the particles and also demands some sort of attractive forces between the solid particles. These same forces influence the consistency of plastic masses. Freundlich (39) emphasizes that plasticity and thixotropy exist when packing is not too close.

When the particles are of a decidedly non-spherical shape,

they display characteristic streaks on stirring showing a persistent layering-effect. Substances which are intrinsically lamellar in structure will display this streaking-effect (40).

Plastic materials can be formed by disintegration of pre-existing aggregates by crushing. The re-aggregation to form a plastic substance occurs between rod-like particles, which set into chains. If the disintegration is carried to a stage at which the rod-like particles themselves are broken down, the chain structures do not form so readily. The elastic properties of plastics, therefore, depend more on their condition of orientation, which is determined by the treatment they receive prior to hardening or setting than on the initial chemical condensation. This theory has been called the "principle of conformation by assemblage" (41).

Colloidal Phenomena

It has been noted that in an amorphous substance, a gradual transformation occurs between the solid and the liquid states. At a certain temperature, therefore, the forces between certain molecules will have been overcome whereas other molecules will still cohere to the solid mass. The result is a mixture of "liquid" and "solid" particles and may be considered an "iso-colloid"; in other words, there are freely moving molecules present near fixed ones. Moreover, if under the influence of heat, molecules of a liquid can combine chemically with one another (either by addition or condensation polymerization) with the formation of larger molecules, complexes will eventually be formed where thermal agitation ceases. Whenever there

are freely moving molecules (i.e. liquid molecules) co-existent with fixed molecules (i.e. solid molecules), an "iso-colloid" is again formed (42,43).

Resins, as a rule, are not composed of single entities but consist of macromolecules of varying size. Resins can thus be considered as gels of highly polymerized organic substances where the disperse phase consists of a highly polymerized form of the material composing the continuous phase. There are also resins which consist of particles of essentially the same size. If all the molecules were of the same size, then one would be dealing with liquids. Inasmuch as it is necessary to assume that in these liquids the particles are of colloidal dimensions, such liquid resins must be considered as sols (43). The particles of such resins which are formed (43) in a liquid medium will then be solvated by the medium.

Another classification which has been made of these high molecular weight organic compounds, is to call them xerogels. (An xerogel is one which has been formed by drying; it consists of the residue remaining after the removal of most of its external or liquid phase.) They are poor in liquid, but are nevertheless coherent (44). The term has been applied to both natural and synthetic resins.

Urea-Formaldehyde Resins

The various condensation products of urea and formaldehyde have been studied since 1919 the world over in endeavors to find products of technical value such as glues, impregnants and molding compositions.

Usually the reaction is carried out in aqueous solution, and the first result is the production of a hydrophilic colloid, which on further condensation, becomes a hydrophobe. It is possible to check the condensation at the hydrophilic (water "soluble") stage and thus produce adhesives and impregnants. The hydrophobe is, of course, ordinarily used for making moldings. In this case the process of thermosetting is carried out by heating at a temperature between 130° and 140°C.

Some typical examples of the preparation of urea-formaldehyde condensation products are as follows.

John (45) prepared a glue by reacting urea and an excess of formaldehyde at a relatively high temperature without adding a condensing agent. Thus five parts of 40% formalin are heated with one part of urea until nearly half of the liquid has been removed by distillation. The glue obtained is highly adhesive. The reaction product can be hardened by heating at 80°C.

Goldschmidt and Neuss (46) found that the proportion of formaldehyde necessary to produce clear resins is reduced by the addition of acid condensing agents. Thus, by heating one hundred grams of 30% formalin with twenty grams of urea and 0.013 gram of hydrochloric acid at 100°C., a transparent product which hardens on prolonged heating is obtained.

On heating one mole of urea with three or more moles of formaldehyde in the presence of a small amount of hydrochloric acid, Rothera, Blythen and Gillespie (47) obtained a gelatinous liquid which solidified when cooled.

Mittasch and Ramstetter (48) found that clear resinous products could be prepared by heating a solution of urea in at

least 2.4 moles of formaldehyde in the presence of dilute acids (e.g. nitric, phosphoric, or acetic acids). If water was then removed by evaporation at a temperature below 50°C., the solution could be considerably concentrated without premature gelation. The product may be hardened at 60-80°C. As an example of the use of this method a warm concentrated solution of six parts of urea, containing the condensing agent, is slowly poured into twenty-five parts of boiling 30% formaldehyde solution. The product is evaporated in vacuo, at a temperature below 50°C., to a syrupy consistency, containing 10-15% water, and is stable for a considerable time. It can then be hardened by continued heating.

Pollak (49) described the use of alkaline condensation catalysts, using weak bases such as pyridine, ammonia, and hexamethylenetramine. In the presence of these substances as catalysts, urea, heated with three moles of formaldehyde, gives after partial evaporation, a syrup which sets at 75°C. to a hard, transparent mass, which is insoluble in both alkalies and acids.

According to Ripper (50) the first stage of condensation may occur in neutral solution e.g., by adjusting the pH to a value of seven. Should the acidity rise above this value, white precipitates are produced which lead inevitably to the ultimate formation of a clouded or opaque resin. At a pH of seven, however, a water-clear solution is obtained. On cooling, cloudy solutions are formed which clear on heating and on prolonged boiling yield viscous masses which harden to clear

resins. In working by this process, either acid-free formaldehyde may be used or ordinary formaldehyde may have its formic acid neutralized by addition of a base. The polymerization of the condensed substance may be brought about by lengthy heating, or more expeditiously, by addition of sufficient acid to raise the pH to about three. The acidity during polymerization should not rise above a pH of about 2.6 since gelation occurs forming a hard white brittle material (containing all the water) and which on standing readily crumbles to a powder.

By this process, thirty parts of urea are condensed by refluxing for a short time with one hundred parts of neutral 30% formaldehyde. Five parts of boric acid dissolved in a little water are added and the mixture is converted into a moderately viscous solution which does not become cloudy on cooling, and which marks the polymerization of intermediates (methylolureas) into a colloidal hydrophilic sol. This may be hardened by evaporating most of the water, casting into molds and heating at 60-100°C. to give a transparent final product. More prolonged boiling of the mixture carries the polymerization further, the clear, hot solution depositing on cooling a white, slimy jelly from which the supernatant liquid may be decanted. The jelly which is opaque, due to adsorbed water, may be dried in vacuo, thereby being rendered transparent. It may be then cast in molds and cured.

A process for the coagulation of the primary condensation product, described by Ripper (51) depends on the flocculation of the substance from dilute solution by further addition of

solvent or by the use of flocculents such as albumin precipitants like phosphotungstic acid. No gelatinization occurs, but the material is obtained as a white amorphous powder which may be molded by heat and pressure. The powder is insoluble in water.

In general, concentration of the reacting mixture is necessary at some stage in order to remove the large excess of water in which condensation takes place. The reaction may, however, be carried out in more concentrated media, solutions containing up to 75% of solid matter (52).being made by dissolving urea in the reagent obtained by the dissolution of the solid formaldehyde polymers in ammonia or alkaline formates. The formaldehyde content of the solution may exceed 40%. On boiling these concentrated reaction mixtures in an open vessel, viscous condensation products are obtained, curing at 100°C. to clear, glassy-masses.

The nature of the chemical reactions taking place during these condensations and during the thermal hardening is extremely complicated, and numerous controls are required in order to establish the conditions necessary for the making of resins which can be converted into molded articles.

Empirical observation played an important part in the development of urea resins. Industrial preparations and techniques, such as those just listed, advanced far more rapidly than the work on the chemistry of the process. It is only as a result of more recent work that much information concerning

the course of the various reactions occurring, has been obtained and structures postulated for the polymerized products.

The Chemistry of the Urea-Formaldehyde Condensation.

The general reaction between formaldehyde and amino-groups entails the formation of methylolamines; these are unstable and lose water forming higher products derived from methyleneamines (53).

$$R\text{-}NH_2 + CH_2O \longrightarrow R\text{-}NH\text{-}CH_2OH$$

$$x\ R\text{-}NH\text{-}CH_2OH \longrightarrow \left[R\text{-}N{=}CH_2\right]_x + x\ H_2O$$

Pulvermacher (54) observed that in acid solution, formaldehyde reacted with benzamide according to the equation:

$$CH_2O + 2H_2N\text{-}CO\text{-}C_6H_5 \longrightarrow C_6H_5\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}C_6H_5$$

Einhorn (55) isolated a different crystalline product, C_6H_5-CO-HN-CH_2OH, which he obtained in acid medium.

The methylol type of structure has since attained great importance in the chemistry of urea resins. Recent studies (56) have shown that the Pulvermacher structure is also often formed. However, it is generally agreed that the methylol compounds are the first condensation products when substances containing amino-groups react with formaldehyde to produce resins.

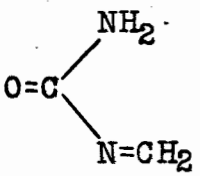
Einhorn and Hamberger (57) were the first to thoroughly investigate methylol compounds. They showed that the composition of the condensation products varied considerably with the conditions of condensation, but that the methylolureas were indeed the first condensation products. Using barium hydroxide as

condensing agent, and neutralizing with carbon dioxide immediately after the initial reaction, di-methylolurea, $CO(NH-CH_2OH)_2$, was isolated as a crystalline, easily soluble body. The compound gives a white amorphous precipitate on standing with dilute mineral acids.

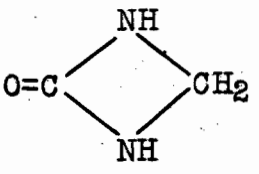
Scheibler, Trostler and Scholz (58) isolated mono-methylolurea, $NH_2-CO-NH-CH_2OH$, when urea was reacted with neutral formaldehyde solution. At an acidic pH a high molecular weight product was obtained instead.

Both of the methylolureas gave off formaldehyde on heating or boiling with water or mineral acids.

A different substance had been obtained from the same materials by Hölzer and Lüdy (59,60,61) in the form of methyleneurea, $C_2H_4N_2O$. This compound was formulated in two different ways namely:



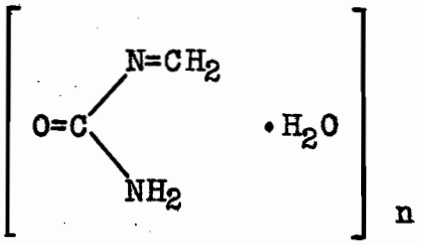
and



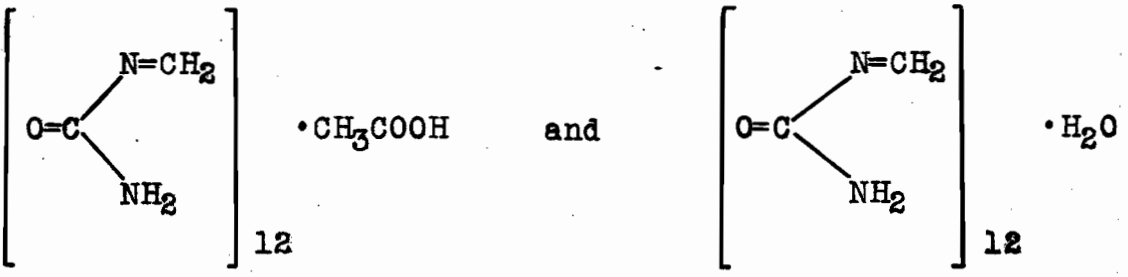
Hölzer Lüdy

While the urea-formaldehyde resins have received considerable scientific study, the reaction of their formation is still not completely understood. It is now generally believed that urea and formaldehyde react reversibly in the presence of acidic and basic catalysts to produce mono-methylol- and di-methylolurea. Further heating of either of these products results in polymer formation.

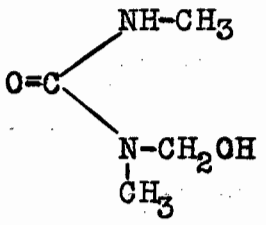
The further stages of condensation were investigated by Scheibler, Trostler and Scholz (62) with the result that the preliminary formation of mono-methylolurea was confirmed. This was found to be transformed by a trace of hydrochloric acid into a high molecular weight product of the same composition. However the polymer is not considered as consisting of methylol units, but rather units of methyleneurea, each containing one firmly bound molecule of water.



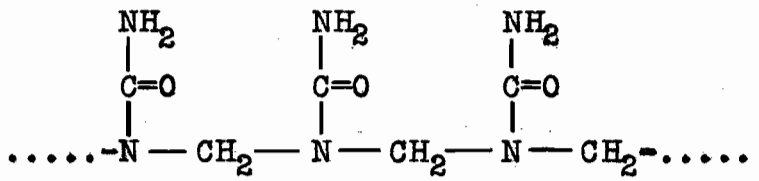
On the other hand, when mono-methylolurea was treated with glacial acetic acid, two well characterized modifications of methyleneurea were obtained. Of the two compounds so produced one is soluble in glacial acetic acid and contains one mole of acetic acid in combination with an average of twelve moles of methyleneurea, whereas the other contains one mole of water in combination with an average of twelve moles of methyleneurea units and is insoluble in acetic acid. Thus:



When symmetrical dimethyl urea was condensed with formaldehyde a monomethylol derivative was obtained (63)

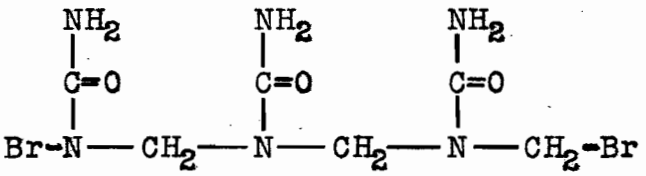


No cyclization or polymerization occurs in this case, a fact which could be interpreted as indicating that the ($N=CH_2$) group is the one which is involved in the polymerization of methyleneurea. Furthermore, the polymerization of methyleneurea may then be readily conceived as a process analogous to that which takes place in the formation of polyoxymethylene long-chain molecules (64) e.g.:

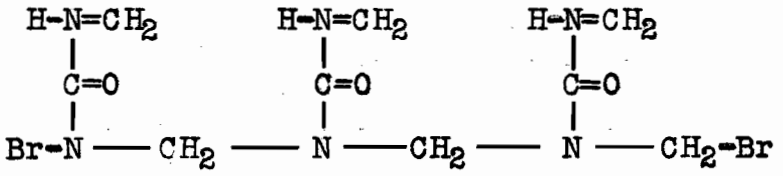


From this formula it may be seen how a molecule of acetic acid or a molecule of water might add to the free valencies at the end of the chains, forming the acetic acid soluble and insoluble compounds already mentioned.

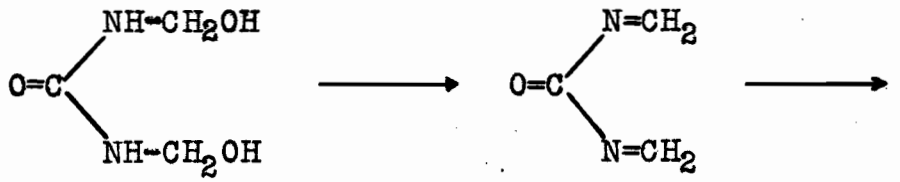
In a similar manner, halogens may add to the polymethyleneurea chains. Such substances formed in glacial acetic acid solutions, according to Scheibler, Trostler and Scholz (65) are not very stable, but give up their halogen on standing in the air, or on slight warming. The loose bromine compound formed in this way contains too little bromine to be a bromamine or bromamide, but corresponds to the bromine addition compound of a trimeric methyleneurea:

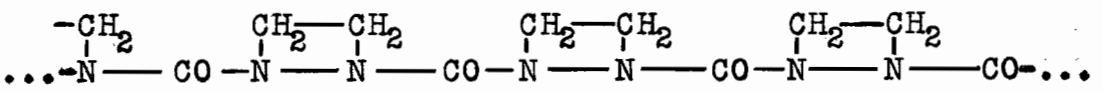


Insoluble compounds are not obtained when di-methylolurea is dissolved in cold acetic acid, but upon addition of an acetic acid solution of bromine, a bromine addition product precipitates. Analysis for bromine indicates that this compound contains three di-methyleneurea residues:

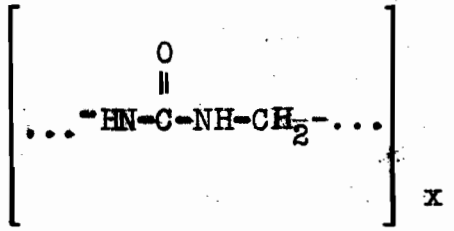


C.A. Redfarn (66) bases his discussion of the importance of maintaining a definite pH during the resin formation upon the fact that aqueous 40% formaldehyde solution almost exclusively used in the manufacture of these resins, contains regularly 0.02 to 0.03% formic acid. He assumes that the succeeding phases of the reaction proceed via the di-methylolurea and di-methyleneurea stages, the latter polymerizing to form chain-like structures. During the hardening process, the chains are supposed to close into cyclic systems:

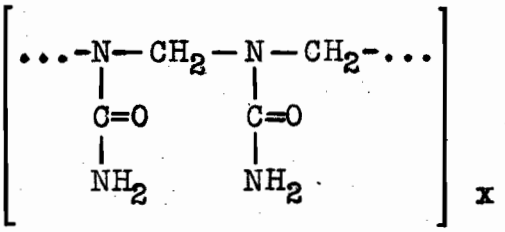




Ellis claims that if the polymerization be considered as proceeding through the methylolureas, the possible product, starting with mono-methylolurea, will be either A or B, according as the primary or secondary amido-nitrogen is the more reactive:

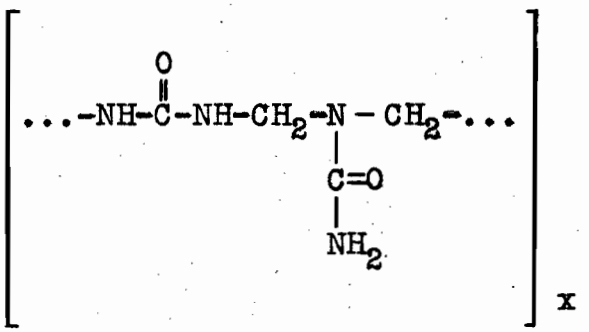


A



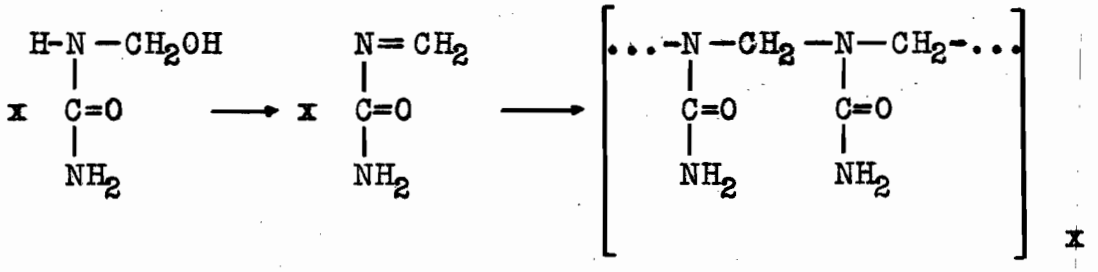
B

The mixed type C is also possible if both nitrogen atoms participate in the polymerization.

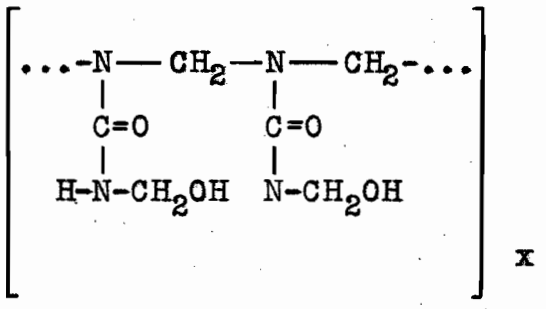


C

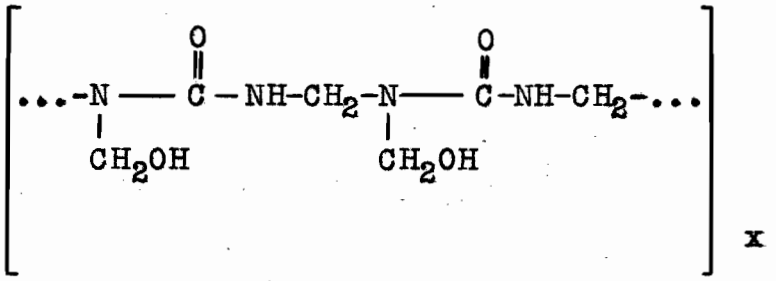
If on the other hand, polymerization proceeds through initial loss of water leading to the formation of methyleneurea, the product could only be of the type B:



In the case of di-methylolurea, the nature of the products and general considerations indicate that the conditions are essentially similar. Chain-formation in this case may be conceived as taking place in two possible ways to yield D and E:

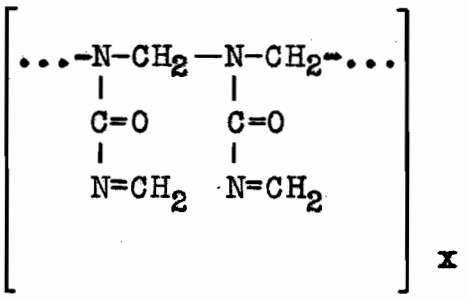


D

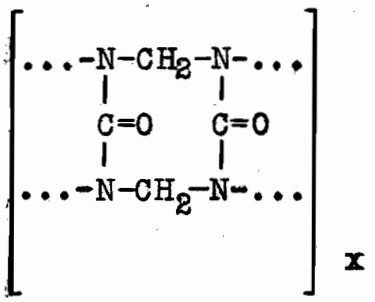


E

or possibly mixed types as before. Since branching may occur at every methylol-group, the formation of long, straight-chain polymers is improbable. If now, the remaining methylol-groups eliminate water giving methylene groups as in F, a redistribution of valencies gives the double-chain G:

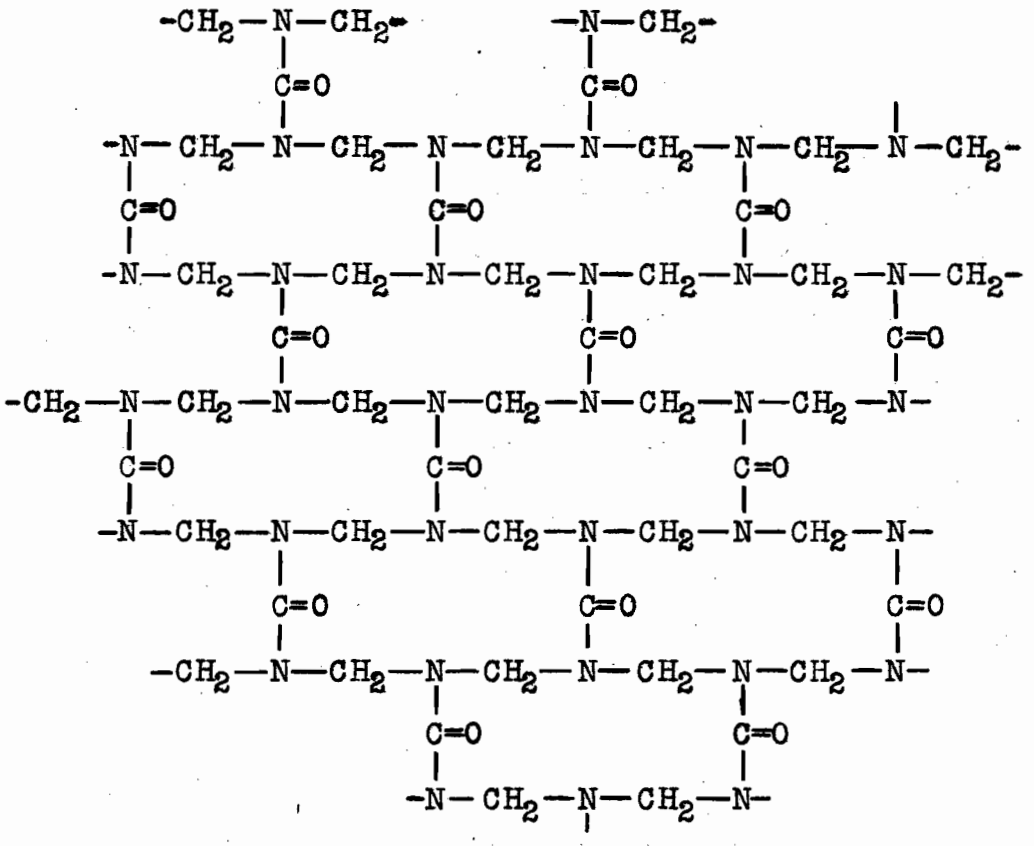


F



G

In the actual condensation process chain branching is inevitable, so that the cured resin, if perfectly orientated, could be represented in the simplest case by the formula:



The outer unsaturated valencies would be attached, in the case of the nitrogen atoms to hydrogen, and in the case of methylene-groups, to hydroxyl-groups. It may be that the acid or basic radicals of catalysts or fillers are chemically attached to the bonds.

Research on the mechanism of the urea formaldehyde resinification was also done by G. Walter and his co-workers (68). He ascertained that the principal factors controlling the progress of the reaction are, the hydrogen ion concentration,

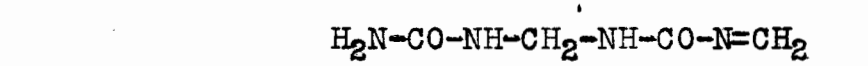
the temperature and the quantitative proportion of the components. In general, hydrogen ion concentrations between 10^{-5} and 10^{-3} and high temperatures were required. The reaction was followed by determining the water given off during the condensation and by estimating the free formaldehyde. The results obtained indicate, according to Walter, that the clear resin consists either of a mixture of monomeric methylene-, dimethylene- and methylene- methylol compounds, or more probably, of urea residues interlinked by methylene bridges and still containing free methylol groups. Assuming a regular type of structure and normal reaction conditions, Walter concluded that there existed an approximately three-membered, one-dimensional "ring chain" carrying one free methylol group. The reaction type is conceived of as a gradually proceeding condensation of methylolurea, not as a polymerization leading through methyleneureas.

In a later publication (69), Walter states that the acid acting as a condensation agent is largely combined at the beginning of the condensation and then released again, so that the hydrogen ion concentration rises to its initial value.

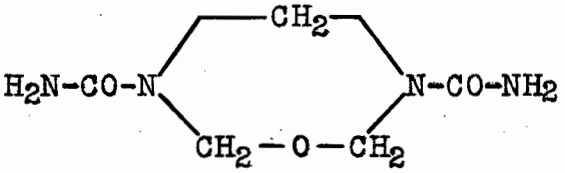
Walter concluded that the condensation of urea and formaldehyde can, according to the conditions of condensation, lead to simple low molecular crystallized products, e.g.: mono-methylol- and di-methylolurea, to amorphous powders, such as methyleneurea, $C_2H_4ON_2$ (Meth. A) or $C_5H_{10}O_3N_4$ (Meth. B) and to resins. He obtained one monomeric Meth. A and one

Meth. B; by fractionation. Further fractions contained only polymers of low molecular weight (dimers and trimers)

monomeric Meth. A.

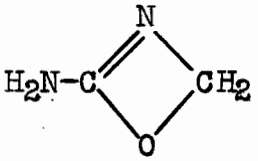


dimeric Meth. A.

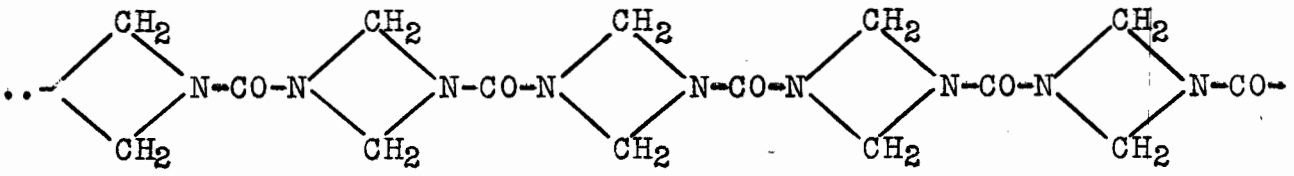


monomeric Meth. B.

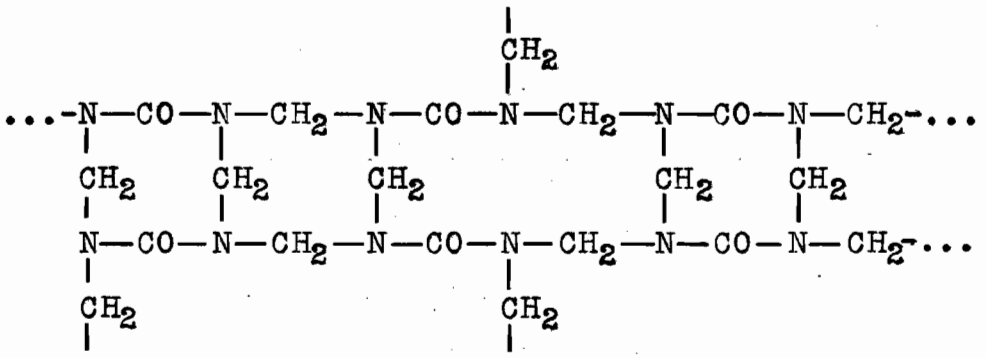
According to Walter, Meth. A exists in both soluble and insoluble form. The latter is produced at high hydrogen ion concentrations and has the following proposed structure:



Walter assumes that the most important constituent of the insoluble and infusible final product of the condensation is a polymer of di-methyleneurea. He formulates one-dimensional ring chains such as:

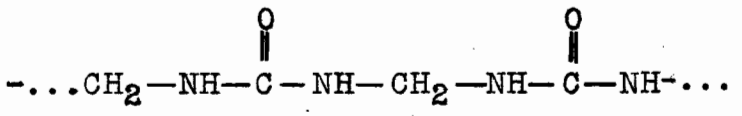


and latticed molecules:

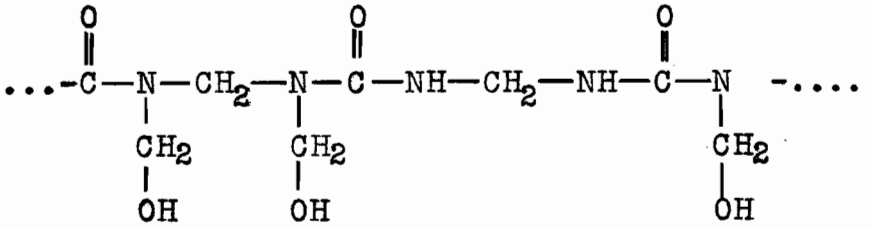


Walter adds that these products also contain Meth. A, Meth. B and strongly combined water.

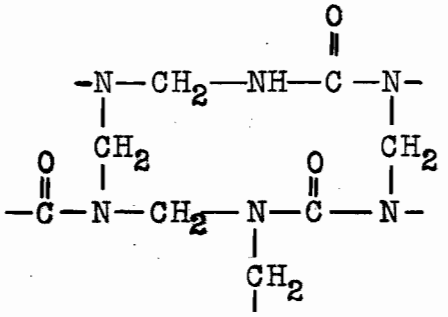
Following the work by Walter, Professor K.H. Meyer (70) maintained that the reactions between urea and formaldehyde ought to be considered from a more general standpoint, without introducing specific formulae. Urea being dibasic, he regards Dixon's water insoluble condensation product (71) formed by acid condensation as a somewhat high molecular polymer having the simple regular formula:



By condensation in the presence of a high proportion of formaldehyde polymers are obtained which dissolve in water, forming very viscous solutions. According to Meyer, it is reasonable to suppose that the solubility in water is promoted by aldehyde-groups attached in such a way to the chains to form polyvalent alcohols of the type:

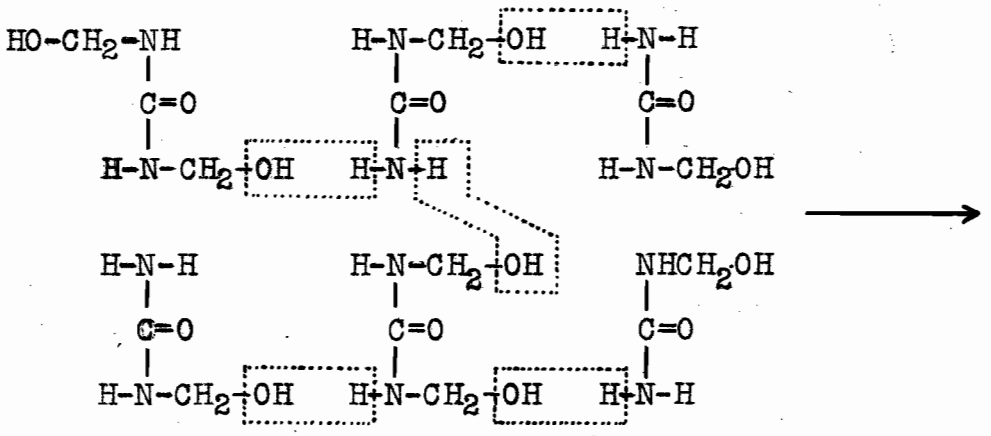


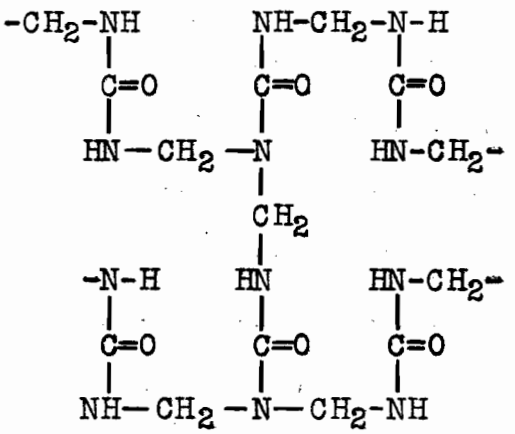
On evaporation glass-like, insoluble masses are obtained, which may be supposed to contain 3-dimensional nets such as:



C.S. Marvel (72) claims that the polymerization proceeds by a stepwise loss of water between the molecules of methylol- and di-methylolurea. Methylolurea liberates formaldehyde on heating, and this may combine with more methylolurea to give di-methylolurea. Hence the polymer produced from pure methylolurea as a starting material will still be very complex.

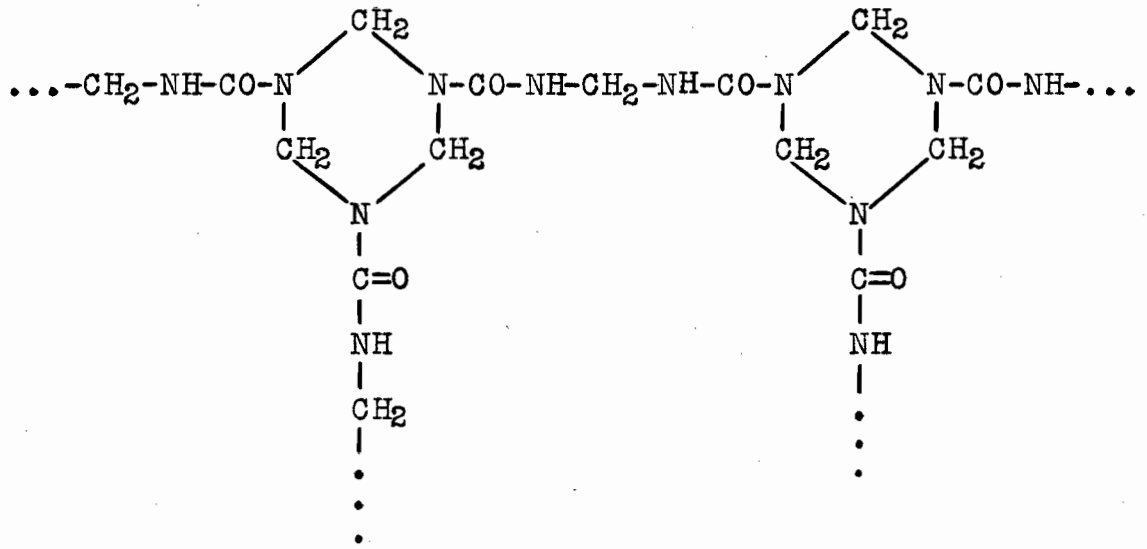
Marvel warns that no strictly accurate scheme for the polymerization reaction can be written, but the following may be considered a possible route from methylol- and di-methylolurea to the final cross-linked polymer.





Although the reaction between urea and formaldehyde has received considerable study and wide industrial use, according to Marvel, so far no structure of the polymeric product is consistent with the fact that urea reacts with formaldehyde to give a polymer whereas none of the substituted ureas will do so.

It has recently been suggested (73) that two principal reactions are involved in the formation of urea-formaldehyde condensation products. Urea shows many properties of an aminoamide. If one of the $-NH_2$ groups is considered to be a primary amine and the other $-NH_2$ group an amide, then their respective reactions with formaldehyde might be predicted as Schiff's base formation and formation of a methylene-bis-amide. Most low molecular weight Schiff's bases trimerize readily. If these reactions occur in the condensation of urea and formaldehyde, the structure of the polymer should be:



If the cyclic intermediate forms first, it leaves three reactive amido-groups to react with formaldehyde. Terminal amino-methylol units would interact on further heating to cause the heat hardening which is characteristic of the product. The known nitrogen content of the polymers agrees with this view of the structure.

The refusal of substituted ureas to give polymers can readily be understood if this structure is accepted. A substituent on the basic nitrogen prevents Schiff's base formation and subsequent trimerization and a substituent on the amido-nitrogen prevents formation of methylene-bis-amide. Hence substitution of any kind in urea will prevent the formation of <u>three-dimensional</u> polymeric products in the reaction with formaldehyde.

de Chesne (74) found that the intermediate stages of the polymerization form highly viscous solutions, which according to de Chesne, display the properties of a highly solvated micelle-colloid. Thus the high viscosity of the solutions is diminished

greatly on heating, and returns to its former value on cooling, whereas molecular colloids show relatively low temperature variation of viscosity. The conclusion is drawn by de Chesne that urea-formaldehyde resins consist of micellular aggregates of linear thread-like molecules of varying degrees of polymerization, which form highly solvated hydrophilic colloids possessing the property of irreversible gelation after curing.

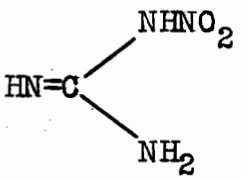
In conclusion, it may be said that the reactions of dibasic urea during condensation with formaldehyde, and also during heat-hardening are extremely complicated. The many possibilities of reaction render research on the mechanism and also on the optimum conditions of the technical process most difficult. The ease with which di-methylolurea is formed, if sufficient formaldehyde is present, alone explains the reason for the number of complications which arise. Di-methylolurea can be considered a tetra-functional molecule which is capable of chain-branching and formation of polymeric networks. Attention may also be drawn to the ease of polymerization either with or without loss of water and finally the readiness with which cyclic structures are formed in the polymerization process.

Although research workers have not investigated the mechanisms of the reactions, formaldehyde reacts with substances related to urea to give useful polymeric products. For example: Guanidine thiocyanate and guanidine carbonate give amorphous resins that may be pressed (75) and dicyandiamide, which is capable of functioning as the urea derivative cyanoguanidine NH_2-C(NH)-NH-CN has been condensed with formaldehyde to give

polymeric products (76,77,78). Pahl (79) was able to isolate the primary condensation product, mono-methyloldicyandiamide, which was found to be a very unstable compound, losing formaldehyde on warming in water solution.

The Chemistry of Nitroguanidine

Nitroguanidine differs from urea in having a nitro-group in place of a hydrogen atom and an imino-group in place of oxygen. Thus:



Nitroguanidine is a powerful explosive remarkable for the fact that it is exceptionally cool. It exists in two crystalline forms (80). The α -form is obtained when guanidine nitrate is dissolved in concentrated sulphuric acid and the solution drowned in water. The α -form is the product used in the explosives industry. It crystallizes from water in long, thin, flat, flexible needles which are difficult to pulverize; N_α = 1.518, N_β = a little greater than 1.668, N_γ = greater than 1.768; double refraction 0.250. β -nitroguanidine is produced by the nitration of a mixture of guanidine sulphate and ammonium sulphate which results from the hydrolysis of dicyandiamide by sulphuric acid. It crystallizes from water in fern-like clusters of small, thin, elongated plates; N_α = 1.525, N_β = (not determined), N_γ = 1.710; double refraction 0.185. It is converted into α -nitroguanidine by dissolving in concentrated sulphuric acid and pouring the solution into water.

Neither form can be converted into the other by solution in water.

Both α - and β -nitroguanidine, if dissolved in hot concentrated nitric acid and allowed to crystallize, yield the same nitrate, thick, rhomb-shaped prisms which melt at 147°C. with decomposition. The nitrate loses nitric acid slowly in air and gives α -nitroguanidine when recrystallized from water.

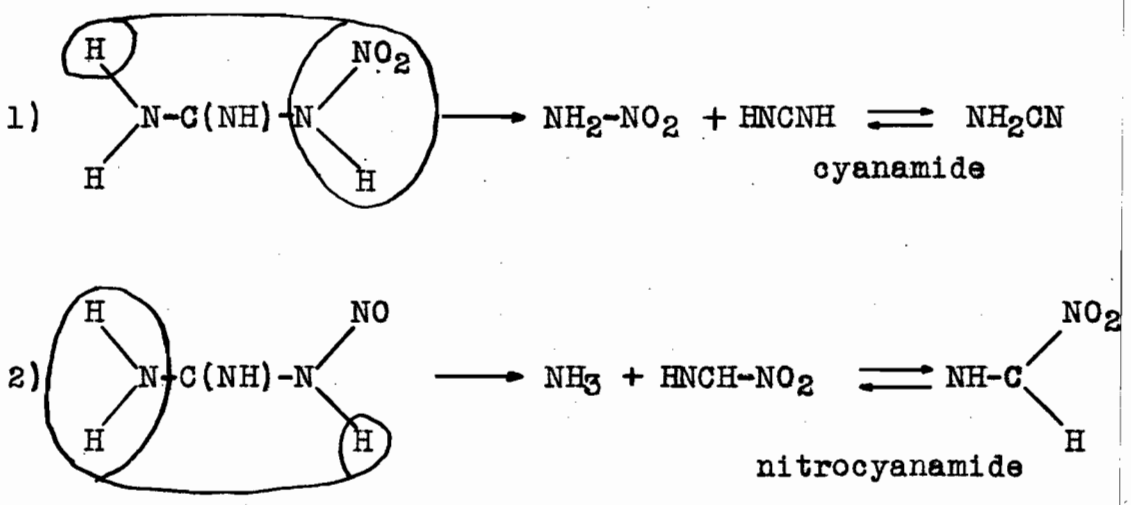
Both forms yield a hydrochloride which crystallizes in needles when recrystallized from concentrated hydrochloric acid. They lose hydrogen chloride rapidly in air and give α -nitroguanidine when recrystallized from water.

The two forms are identical in all their chemical reactions, in their derivatives and color reactions. Both forms melt at 232°C. if the temperature is raised with moderate slowness, but by varying the rate of heating, melting-points ranging between 220°C. and 250°C. may be obtained.

Solubilities of nitroguanidine: In water at 100°C., 10.366 g. per 100 ml. In methanol and ethanol, very slightly soluble. In benzene, ether chloroform, carbon disulphide and carbon tetrachloride, insoluble.

Many of the reactions of nitroguanidine, particularly its decomposition by heat and the reactions which occur in aqueous and in sulphuric acid solutions, follow directly from its de-arrangements (81).

Nitroguanidine de-arranges in two ways (81), as follows:



On heating, a solution of nitroguanidine in concentrated sulphuric acid comports itself as if the nitroguanidine had de-arranged into nitroamide and cyanamide. Nitrous oxide containing a small amount of nitrogen comes off first (from the dehydration of the nitroamide), and carbon dioxide (from the hydrolysis of the cyanamide) comes off later and more slowly. Long continued heating at an elevated temperature produces carbon dioxide and ammonia according to the equation:

$$NH_2\text{-}C(NH)\text{-}NHNO_2 + H_2O \xrightarrow{H_2SO_4} N_2O + (NH_4)_2\,SO_4 + CO_2$$

A solution of nitroguanidine in concentrated sulphuric acid, after standing for some time, no longer gives a precipitate of nitroguanidine when it is diluted with water.

H.S. Fry and J.F. Treon (82) found that the decomposition of nitroguanadine with sodium hydroxide is quantitative according to the equation:

$$2NaOH + NH_2\text{-}C(NH)\text{-}NH\text{-}NO_2 \longrightarrow Na_2CO_3 + 2NH_3 + N_2O$$

In aqueous solution nitroguanidine de-arranges in both of the above modes, but the tendency toward de-arrangement is small unless an acceptor for the product of the de-arrangement is present. Therefore nitroguanidine is quite stable in aqueous solution; but after numerous boilings and recrystallizations the same solution becomes ammoniacal. Ammonia being alkaline, tends to promote the decomposition of nitroamide in aqueous solution. Further, because of its mass action effect, it tends to inhibit de-arrangement in the second mode which produces ammonia. If nitroguanidine is heated with an aqueous solution of ammonium carbonate, nitrous oxide comes off rapidly, the ammonia combines with the cyanamide from the de-arrangement.

T.L. Davis and R.C. Elderfield (83) showed that de-arrangement of nitroguanidine and substituted nitroguanidine increases as the pH increases. Increasing hydrogen ion concentration has the property of inhibiting the de-arrangement.

In the presence of a primary aliphatic amines, nitroguanidine in aqueous solution de-arranges in the second of the above indicated modes, ammonia is liberated and the nitrocyanamide combines with the amine to form an alkyl nitroguanidine.

$$HNCN\text{-}NO_2 + CH_3\text{-}NH_2 \longrightarrow CH_3\text{-}NH\text{-}C(NH)\text{-}NH\text{-}NO_2$$

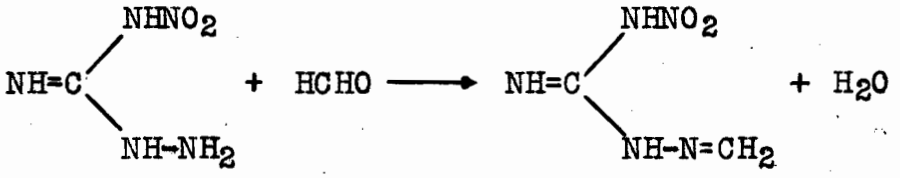
nitrocyanamide methyl nitroguanidine

The structure of the N-alkyl, N'-nitroguanidine is demonstrated by the fact that it yields the amine and nitrous oxide by hydrolysis, indicating that the alkyl group and the nitro group

are attached to different nitrogen atoms.

The same N-alkyl, N'-nitroguanidines are produced by the nitration of the alkyl guanidines. Davis and his co-workers (83,84) showed that whereas in substituted nitro-ureas the substituent group may be attached to the same nitrogen atom as the nitro-group, in substituted nitroguanidines the substituent is always on the non nitrated amino-group.

Nitroguanidine, warmed with an aqueous solution of hydrazine, yields N-amino-, N'-nitroguanidine (85). Philips and Williams were able to isolate a condensation product of nitroaminoguanidine and formaldehyde according to the following:



This methylene nitroaminoguanidine crystallized out by allowing a saturated solution of nitroaminoguanidine to stand with a 37% formaldehyde solution.

Nitroguanidine decomposes immediately upon melting and cannot be obtained in the form of a liquid, as can urea and dicyandiamide. A small quantity heated in a test-tube yields ammonia, water vapour, a white sublimate in the upper part of the tube, and a yellow residue of mellon. The products which are formed are those which would be expected from the dearrangement (86) namely, water and nitrous oxide (from nitroamide), cyanamide, melamine (from polymerization of cyanamide), ammonia, nitrous oxide again and cyanic acid (from nitro-cyanamide), cyanuric acid (from the polymerization of cyanic acid),

ammeline and ammelide (from the co-polymerization of cyanic acid and cyanamide) and from the interaction and decomposition of these substances, carbon dioxide, urea, melam, mellon, mellem, nitrogen, prussic acid, cyanogen and paracyanogen. All of these substances have been detected in, or isolated from, the products of the decomposition of nitroguanidine by strong heating.

Picrates have long been favorite derivatives for the characterization of nitrogen bases. Mitchell and Bryant (87) have prepared picrates of such amines as R_2NH, $R\text{-}NH_2$, R_4N^+, $(CH_2)_6N_4$, $R_2N\text{-}C_2H_5OH$ and guanidine. Kopeller (88) formed the picrate of guanidine and dicyandiamide for identification. Guanidine picrate was once used as a projectile explosive (89). Davis and Rosenquist (90) have prepared picrates of many derivatives of guanidine. Nitroguanidine picrate can be prepared using ammonium picrate solution saturated with guanidine picrate as a solvent for nitroguanidine. Davis says that it is less likely that the acid in nitroguanidine salts is attached to the nitrated amino-group than to the more basic one.

THEORETICAL INTRODUCTION

The Colloidal Nature of High Polymers

Attention is often called to the lyophilic-colloidal nature of certain high polymers. Examples of such polymers are: the hydrophilic sols of linear urea-formaldehyde condensation products (before thermal hardening); proteins, such as gelatin and albumin; saccharocolloids, such as starches and gums; and organophilic sols, such as rubber in benzene, vinyl acetate and nitrocellulose in various organic media. These polymeric substances have the common property of being composed of chain molecules, and we have seen that such linear polymers can indeed be distinguished from cross-linked polymers by the fact that solutions of chain molecules display the properties of a sol. Further the discussion on the colloidal nature of resins indicated that this polymeric state can be considered as a gel, and since the formation of gels is characteristic of lyophilic colloids, it is therefore possible to regard resins as lyophilic-colloidal systems in which the internal-phase particles and external phase are intimately associated.

For these reasons it would be advisable to study in some detail, lyophilic colloids and the properties which such systems would be expected to exhibit, and to stress the colloidal nature of resins for the elucidation of the arrangement of the molecules in this state.

The viscosity of lyophilic systems is much greater than that of the dispersing medium (91,92). The reason for this behaviour lies in the fact that lyophilic colloids, as distinct from lyophobic colloids, are without exception substances which become solvated with the dispersing medium. The molecules of the lyophilic colloids are complicated and large and become solvated as single molecules or as small groups of molecules to form lyophilic micelles. The solvated character of lyophilic micelles, in which some of the molecules of the external phase are closely and intimately affixed, accounts for the viscosity of lyophilic-colloidal systems. As a result of this intimacy of phases, lyophilic systems do not possess the property of scattering light (the Tyndall effect) to so pronounced a degree as lyophobic systems (93).

While the stability of lyophobic sols depends essentially upon the existence of surface charges that have a mutually repelling action when the particles collide, the stability of lyophilic sols depends essentially on the solvated character of the colloid, in which the adsorbed solvent forms a protective layer about the particles. In many instances the removal of this protective layer is sufficient to cause coagulation of the desolvated particles.

The protective action of the solvation of particles is clearly indicated by the experiments of Kruyt and his co-workers (94). When dehydrating agents such as alcohol are added to an agar sol, the viscosity of the sol decreases. As a result the sol behaves

somewhat like a lyophobic sol; for example: in addition to a decrease in viscosity, the optical properties become like those of a lyophobic sol; the agar sol becomes bluish and the indistinct Tyndall cone of the original lyophilic sol changes to a well-defined picture.

Often it is possible to produce a gel by adding, gradually to a lyophilic-colloidal sol, a second solvent in which the lyophilic colloid is much less soluble, though if the process is carried out too rapidly, a precipitate instead of a gel is likely to result (95). The action of any such second solvent in causing gelation is regarded as desolvation of the lyophilic colloid, resulting in the formation of internal-phase particles possessing sufficient surface to adsorb the molecules of the liquid medium.

The formation of gels is characteristic of lyophilic colloids. When such conditions as concentration and temperature are favourable, the lyophilic systems are said to change from a sol to a gel. This change is evidenced by the formation of a semi-solid gelatinous-mass rich in external phase. The term, plastogel has been offered by Wagner (96) for a gelatinous system possessing plasticity. When the external phase of a lyophilic-colloidal system, such as a sol or a plastogel, is removed by evaporation or desiccation to leave a dried residue an xerogel is said to have been formed (97). The term xerogel has been applied to resins. They are gels which are extremely poor in external phase since most of the dispersing medium has been removed, yet they maintain their plasticity and remain coherent.

Many such lyophilic systems become "fluid" when their temperature is increased above a certain range and gel again when the temperature is reduced below this range. Such gels are said to be heat-reversible. Wagner (96) suggests that the term viscogel be applied to those which when "melted" yield a sol of high viscosity; for example: gelatin is a heat-reversible viscogel.

Many gels will absorb appropriate liquids, with the result that they increase in volume until eventually they go into solution. This phenomenon is called swelling.

If swelling is unlimited in this fashion, it may be concluded that the solvent penetrates between the free chains or micelles forcing them apart until complete solution is brought about.

In some instances it is necessary to add a quantity of a suitable peptizing agent, which is usually a polar medium, to effect solution. In these cases, the chains are said to be held together by strong van der Waal's forces, that is, they are held together by associated dipoles or by hydrogen bonds (98).

In other cases primary valence bridges are present between neighboring chains and the polymer is cross-linked. When such is the case, swelling is limited and solution can only be effected by destroying these cross-links by chemical methods.

Freundlich and Juliusburger (99) call attention to another phenomenon of lyophilic colloids called rheopexy, i.e., when a colloidal system consists of internal-phase particles of a laminar or fibrillar shape, gelation is greatly hastened by slow but pronounced elliptical stirring. Such motion apparently brings about

a parallel alignment of the internal-phase particles that aids gelation.

In a lengthy series of experiments, Katz (100,101) studied the effect of swelling of many gels by means of the X-ray spectrum. Were the swelling process one of taking up the liquid intermolecularly, that is, a solubility process, the dimensions of the lattice as shown by the X-ray spectrum would be increased. On the other hand, if the liquid taken up were intermicellularly dispersed, the dimensions of the lattice as shown by the X-ray patterns would remain unchanged. Katz found that no change in the X-ray spectrum occurred on swelling, an indication that instead of the liquid being taken up intermolecularly, it was taken up intermicellularly. This fact seems to prove that the structure of gels is micellular in nature.

Meyer (102) claims the formation of the framework in gels is due to a kind of crystallization. According to Meyer, in all reversible gels which have been studied as yet, the specific heat increases considerably in the region of temperature over which gelation or alternatively liquefaction occurs. On gelation, therefore, latent heat is set free--degrees of freedom are frozen. It is further claimed that X-ray analysis has demonstrated the presence of ultramicroscopic crystallites in many gels.

Gerngross, Hermann and Abitz (103,104) claim that the "molecules" taking part in crystallizations are only portions of chains; other portions remain amorphous or, more correctly, dissolved, that is, surrounded by solvent to give what are termed "fringed" micelles.

The theory that the formation of gel or the transformation of a sol to a gel is a sort of crystallization that produces a lattice or network wherein the crystalline threads are associated with the dispersing medium is held by a number of other investigators (105,106). Others regard the colloidal particles as being linked together or agglomerated to form a filamentous structure not necessarily crystalline in nature (107).

Regardless of the exact character of the internal phase, that is, whether it is crystalline or amorphous, the data available lead to the conclusion that the structure of gels is fibrillar or micellular in nature.

Syneresis, which may be defined as the exudation of the liquid constituent of gels irrespective of the vapour pressure, is a common occurrence; in fact, all gels will synerize to some extent on standing. As a result, the gel undergoes a certain amount of shrinkage. However, the total volume of the system remains the same since the volume of exuded liquid is found to be equal to the loss in volume of the gel (108).

Since the total volume remains the same, the exuded liquid must result from the release of liquid held in the fibrous network of the gel, and regardless of the extent of exudation with respect to gel concentration, it can be said that syneresis is a continuation of the gelation process in which the fibres or micelles come more closely associated resulting in a decrease of the active surface.

In the same way, the transformation of a sol to a plastogel then to an xerogel or resin, may be regarded as a continuation

of the gelation process. During this transformation the fibrous or micellular structure is probably growing through aggregation with a continuous decrease in active surface for the adsorption of external phase.

In conclusion it may be said that resins have a compact fibrous or micellular structure in which there is relatively little surface for the adsorption of the fluid medium.

EXPERIMENTAL

pH Limitations in the Nitroguanidine-Formaldehyde Reaction

Early in the investigation it was found necessary to maintain a pH control when nitroguanidine-formaldehyde reaction products were formed in water solution. The degree of acidity or alkalinity of the reaction mixture, as well as the duration of heating markedly affected the type of condensation product.

The following will introduce the experimental section and will serve to show the necessity of forming nitroguanidine-formaldehyde high polymers in an acid medium.

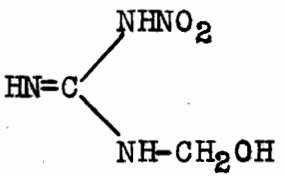
A mixture of 52 g. (0.5 mole) nitroguanidine and 122 g. (1.5 mole) formaldehyde (as 37% formalin) in 122 ml. water was refluxed at 96°C. for 20 minutes, during which all of the nitroguanidine went into solution. The pH of the reaction mixture was 3.67 before heating, due to formic acid present in the formalin. The reaction solution was cooled to room temperature and a white condensation product crystallized out in short platy crystals.

The crystalline condensation product could not be recrystallized from warm solvents without decomposition. After washing with cold 10% aqueous methanol and drying to constant vapor pressure over calcium sulphate, this compound was analysed in the Microchemical Laboratories of the University of Toronto with the following results:

Calcd. for $C_2H_6O_3N_4$: C, 17.81; H, 4.44; N, 41.4%

Found: C, 18.4, 18.3; H, 4.41, 4.42; N, 41.8, 41.1%.

This condensation product was later shown to be monomethylolnitroguanidine.



In other runs, the hot reaction solution was cooled to room-temperature; the pH was adjusted to 2.6 with chloracetic or phosphoric acid, and heating was continued for 4 hours. The solution was then evaporated, by removing the reflux condenser, until a viscous syrup was obtained, which could be cured at 90°C. to a white, opaque, thermoplastic resin.

Partial evaporation gave a solution which was poured into cold water to precipitate the polymer as a white amorphous powder. After washing with water and drying in a desiccator, the powder was found to be moldable.

The final product in both cases burned rapidly and vigorously when ignited and left a charred residue.

Several attempts were made to mold this polymeric powder into buttons, using a hydraulic plastic press and an electrically heated die. The softening-point of the powder was determined in a melting-point tube, and at 126°C. the material began to flow.

Experiment showed that the best molding temperature was between 110°C. and 145°C.; below 110°C. the powder would not flow and above 145°C. it flowed too freely. Pressures ranging from 1,000 to 4,000 lbs./sq. in. were applied from one to five

minutes. In all moldings the powder tended to stick do the die and produce rough, brittle grains. The use of "fillers" such as pyroxylin, "plasticizers" such as camphor, and high-temperature lubricants such as canauba wax failed to overcome the defects.

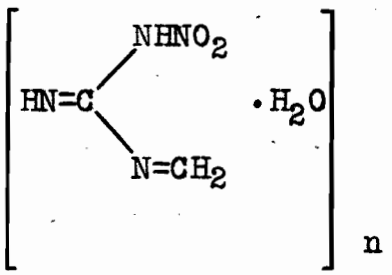
Extrusion through a die at temperatures ranging from 120-165°C. and pressures ranging from 3,000 to 5,000 lbs./sq.in. produced cords which exhibited good burning qualities, but were brittle and rough in texture.

Samples of the molding powder were analysed in the Microchemical Laboratories of the University of Toronto with the following results:

Calcd. for $(C_2H_6O_3N_4)_n$: C, 17.81; H, 4.44; N, 41.4%

Found: C, 18.3, 18.0; H, 4.13, 4.31; N, 41.2, 41.5%.

It can be seen from the analytical results that the finished polymer, insofar as percentage composition is concerned, is identical with the primary condensation product, mono-methylolnitroguanidine. It is difficult to account for a polymer with units of the same elementary composition as mono-methylolnitroguanidine. However, the polymer was not considered as consisting of methylol units, but rather of units of methylenenitroguanidine containing one firmly bound molecule of water:



This consideration is analogous to the structure given to a

polymer from mono-methylolurea, obtained by Scheibler, Trostler and Scholz (62) under similar conditions.

Ripper (109) also obtained under similar conditions a white polymeric product from urea and formaldehyde containing all the water originally present.

Hydrogen ion concentrations less than 10^{-3} caused decomposition of nitroguanidine during the four hours continued heating of the reaction solution; the more basic the solution the more extensive the decomposition. For example: after four hours heating under reflux at pH 4-5, evaporation of the reaction solution gave a viscous syrup which set to an opaque gel on cooling. Microscopic examination showed the presence of some short platy crystals which were probably mono-methylolnitroguanidine. At 90°C. the gel was converted to a brittle, clear, yellow-brown resin having a strong amine odour and which burned very poorly after difficult ignition.

At pH 7-10, evaporation of the reaction solution after four hours heating under reflux, gave a viscous syrup which cured to a dark brown resin, smelling strongly of ammonia and cyanide. The cured product would not ignite. It was observed that considerable gassing of the reaction solution took place at hydrogen -ion concentrations less than 10^{-7}.

De-arrangement of nitroguanidine was considered to have taken place at these pH values. According to Davis (81), nitroguanidine de-arrangement is particularly noticeable the more alkaline its solution or if an acceptor for the products of de-arrangement is present. Several substances capable of reacting

with formaldehyde can be obtained by interaction of de-arrangement products e.g. melamine cyanamide and dicyandiamide. In this way, formaldehyde was considered to act as an acceptor for the products of de-arrangement to form resins during the prolonged heating period, in which the nitro-group of nitroguanidine was no longer present.

Primary Condensation Products

It is now generally agreed that the two factors which most influence the course of reactions between formaldehyde and members of the urea family are: (a) the pH of the condensing medium and (b) the ratio of formaldehyde to the other component.

Attention may be drawn especially to the tendency to form methylol compounds to which all subsequent reaction products can be related.

By analogy it is to be expected that the nitroguanidine-formaldehyde reaction would be similarly conditioned and that the primary condensation product would be a methylolnitroguanidine.

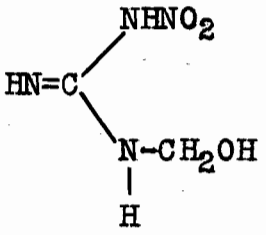
For this reason it was decided to attempt analyses of the simplest products formed during the earliest stage of reaction. Accordingly one mole of nitroguanidine was reacted under standard conditions with 37% formaldehyde solution containing 0.5, one, two, three and four moles of formaldehyde. The pH of the four solutions was constant, the temperature was constant and the volume of each solution was made constant by adding 10% aqueous methanol; thus the concentration varied.

In each case the reagents were introduced into a one-litre

three-necked flask equipped with a mercury-seal-stirrer, a reflux condenser and a thermometer. All joints were ground-glass. The reaction mixture was refluxed until a clear solution resulted; then about 15 ml. methanol were added to assure the stability of excess formaldehyde, and the contents were allowed to cool to room-temperature. In each case white platy crystals were precipitated and were filtered off. After washing with a small quantity (ca. 150 ml.) of cold 10% aqueous methanol, the precipitate was dried to a constant vapour pressure in a desiccator over calcium sulphate. This technique of purification was the only one possible, since it was found that the material was extremely unstable; on dissolving in warm water formaldehyde was evolved, and on recrystallization from methanol several times, only needles of nitroguanidine were obtained.

Formaldehyde and ammonia analyses were carried out on the reaction products according to the method of Connor et al (110), and the results are given in Table I below.

Thus from the analytical results it would seem that the first condensation product of one mole of nitroguanidine with two, three and four moles of formaldehyde is mono-methylolnitroguanidine;



where the theoretical requirements of ammonia and formaldehyde are 12.6% and 22.4% respectively. No other simple product of

TABLE I

Run No.	Nitro-guanidine in moles	CH_2O in moles	Temp. in °C.	Time of solution in min.	Initial pH of solution	Final pH of solution	Approx. Yield in g.	NH_3 in %		CH_2O in %	
1	1	1	96	60	3.75	3.75	65	14.1	14.0	13.1	13.1
1a	1	1	96	60	3.75	3.75	70	13.1	13.9	12.1	11.8
2	1	2	96	25	3.65	3.65	50	12.2	11.8	24.7	26.0
3	1	3	96	20	3.6	3.6	40	12.6	12.5	23.3	23.3
4	1	4	96	15	3.6	3.6	40	12.4	12.4	23.3	23.1
5	1	0.5	96	(a)	3.7	4.1	..	15.5	14.9	14.1	14.6

(a) incomplete after 240; unreacted nitroguanidine filtered off before cooling.

condensation, considered as possible, approaches the analytical figures listed above. The formation of methylolnitroguanidine is, moreover, to be expected in view of the known, simple, methylol compounds of urea, thiourea, dicyandiamide and other members of the urea family.

However, when only one mole of formaldehyde is present it would seem that another product is obtained. The yield is greater indicating less solubility in the medium, and the formaldehyde content is significantly lower. Here it was tentatively concluded that two equivalents of nitroguanidine had reacted with one equivalent of formaldehyde to produce methylene-bis-nitroguanidine

$$O_2N-HN-\underset{\underset{NH}{\|}}{C}-NH-CH_2-NH-\underset{\underset{NH}{\|}}{C}-NH-NO_2$$

where the theoretical requirements of ammonia and formaldehyde are 15.5% and 13.7% respectively. Under these conditions of reaction where the concentration of formaldehyde is much less than in runs Nos. 2, 3 and 4, it is possible that mono-methylolnitroguanidine is first formed, followed by loss of water with a molecule of nitroguanidine to give methylene-bis-nitroguanidine. This would account for the increased yield, since methylene-bis-nitroguanidine would be expected to be less soluble than methylolnitroguanidine, in the medium. Moreover, this structure is analogous to the Pulvermacher structure for reaction products obtained from the reaction between benzamide and formaldehyde, and urea and formaldehyde.

Elementary analyses for carbon, hydrogen and nitrogen were

carried out in the Microanalytical Laboratories of the National Research Council, Ottawa, and the results are in reasonably good agreement with the proposed structures for mono-methylolnitroguanidine and methylene-bis-nitroguanidine considering that scrupulous purification was not possible.

Methylene-bis-nitroguanidine:

Calcd. for $C_3H_8O_4N_8$: C, 16.20; H, 3.64; N, 51.90%.

Found: C, 16.07, 16.00; H, 4.57, 4.52; N (Dumas) 47.28, (HI) 44.84%.

Mono-methylolnitroguanidine:

Calcd. for $C_2H_6O_3N_4$: C, 17.81; H, 4.44; N, 41.40%.

Found: (CH_2O: nitroguanidine::2:1) C, 18.15, 18.29; H, 4.96, 4.83; N, 41.09%.

(CH_2O: nitroguanidine::3:1) C, 18.40, 18.40; H, 4.97, 4.84; N, 40.62%.

(CH_2O: nitroguanidine::4:1) C, 18.87, 19.08; H, 4.91, 4.70; N, 39.91%.

In reporting these values, G. Barker, of the National Research Council, states in part .."we have encountered a great deal of difficulty in the nitrogen analyses, and although we have tried both the recognized methods we have been unable to obtain satisfactory results".

Molecular weight determinations according to the method of Clark (111) were carried out at room-temperature in 100% formic acid as solvent. The technique developed for the preparation of absolute formic acid was vacuum distillation of the acid after standing in a closed system over boric anhydride. Reagent for-

mic acid contains approximately 10% water after treatment with anhydrous calcium sulphate. The final traces of water, however, are too firmly held to be removed by ordinary drying agents; boric anhydride was found to be efficient for this purpose, and was prepared by heating boric acid in a platinum crucible to 800°C. in an electric furnace.

Molecular weight values for methylene-bis-nitroguanidine were obtained as follows:

Calcd. for $C_3H_8O_4N_8$: mol. wt. 210; Found: 183, 186, 189.

The molecular weight values of the first reaction product of nitroguanidine in the presence of two moles (or more) of formaldehyde agree well with the molecular weight calculated for mono-methylolnitroguanidine:

Calcd. for: $C_2H_6O_3N_4$: mol. wt. 134; Found: 138, 138.

Thus it would appear definite that when nitroguanidine condenses with formaldehyde in aqueous medium at a pH of about 3.6, either methylene-bis-nitroguanidine or mono-methylolnitroguanidine are first formed, depending on the relative proportions of the reactants; but that mono-methylolnitroguanidine is indeed the first condensation product.

Polymerization of Mono-methylolnitroguanidine in the Presence of Picric Acid

A study of various acid condensing reagents, in the preparation of urea-formaldehyde resins, was made by Ellis (112), and it was found that acids have a tendency to form resinous complexes by combining with the condensation product. For this reason it was decided, that in the preparation of explosive polymers from nitroguanidine and formaldehyde, the use of highly nitrated acids would impart advantageous properties. Picric acid was found to be a suitable condensing agent for these preparations.

The separation of mono-methylolnitroguanidine in the solid form is not necessary in the formation of a nitroguanidine-formaldehyde polymer. It is possible to effect preliminary condensation as far as methylol formation, then to polymerize this condensation product by the addition of picric acid.

The first stage of the reaction must occur at a pH of about 3.6 and at a temperature of 96°C. Commercial, 37% formalin usually contains enough formic acid to give this pH value. Should the acidity fall much below this value, decomposition of nitroguanidine takes place, which, as already pointed out, leads to the ultimate formation of a resin of poor burning qualities. At a pH of 3.6, however, a water-clear solution of mono-methylolnigroguanidine is obtained with not less than 2 moles of formaldehyde present per mole of nitroguanidine. Polymerization of the mono-methylolnitroguanidine is brought about by the addition of sufficient picric acid to lower the pH to at least 2.5.

By this process, a mixture of 104 g. (1 mole) nitroguanidine, 246 g. 37% formalin (3 moles formaldehyde) and 82 g. water was introduced into a one-litre, three-necked-flask, equipped with a mercury-seal stirrer, a reflux condenser and a thermometer. All the joints were ground-glass. The reaction mixture was refluxed at 96°C. for 25 minutes, at which time a water-clear solution resulted; then 20 g. (0.088 mole) picric acid were introduced and the mixture refluxed for a further period. After three hours the reaction mixture was converted into a clear, orange, "moderately" viscous solution which, on cooling deposited an orange, hydrophobic plastogel, from which the supernatant liquid was decanted. The name N.G.F.P. was given to this reaction product. On drying at 100°C. N.G.F.P. gave a clear, brittle, glass-like mass or resin.

Properties of N.G.F.P.

Thermoplasticity

Cured N.G.F.P. was found to be a thermoplastic resin and hence a chain polymer. The "softening-" or "melting"-point was determined as the temperature at which a sample of the resin began to flow in a constriction of a large melting-point tube, at atmospheric pressure.

By this procedure the "softening"-point was found to rise from 25°-30°C. to 150°-155°C. during curing at 100°C. for 10 hours. The process of curing in this instance was one of heating to a maximum "softening"-point. Thus, continued heating failed to

raise the "softening"-point beyond the value of 150-155°C. The curing treatment converted the soft N.G.F.P. gel to a clear, brittle, orange resin.

In an attempt to raise the "softening"-point or to impart thermosetting properties to N.G.F.P., a small amount of urea (4.2 g; 4% by weight of nitroguanidine) was added to the preparation. The resultant polymer was similar to N.G.F.P. in physical properties; however, its "softening"-point was raised to 165-170°C. on curing.

Explosive Power

A sample of cured N.G.F.P. was examined in the Beloeil Works of Canadian Industries Limited and the following results reported.

When a 10-g. sample was fired with a No. 8 cap in the ballistic mortar, detonation was complete, some fumes were evolved and a deflection of 13.2° was recorded, equivalent to 61% that of T.N.T.

A 10-g. sample of the polymer which had its "softening"-point raised to 165-170°C. by the addition of urea, gave incomplete detonation, fumes were evolved and some unexploded material remained in the chamber.

No detonation was occasioned in the Fall-Hammer Test using a torpedo at a vertical height of 180 cm. on either of the above polymers.

It was deduced that little or no de-arrangement of the nitroguanidine occurred during the preparation of N.G.F.P., since the ballistic mortar gave an explosive force 0.61 times that of

T.N.T., which cannot be accounted for on the basis of picric acid, retained as a resinous complex, alone.

In order to ascertain whether N.G.F.P. contained any free picric acid, a small amount (ca. 10 g.) of the pulverized resin was extracted with 150 ml. ethanol in a Sohxlet apparatus for 18 hours. Upon evaporation of the solvent to dryness, no trace of picric acid could be found. It was thus concluded that picric acid had entered into a resinous complex, such as Ellis found when using acid condensing agents in the preparation of urea-formaldehyde resins.

Solubility

N.G.F.P. was found to be insoluble in water and ether; but acetone, nitromethane and concentrated hydrochloric acid solution could be made of various concentrations and viscosities. It was found that the solubility in acetone and nitromethane became increasingly difficult as the "softening"-point was raised from 25-30°C. to 150-155°C.; N.G.F.P. of "softening"-point 25-30°C. dissolved at room-temperature by stirring, whereas if the "softening"-point was 150-155°C. several hours of refluxing were required to effect solution. In concentrated hydrochloric acid, N.G.F.P. was dissolved at room-temperature by stirring regardless of the "softening"-point.

An acetone solution of N.G.F.P. was evaporated to a syrupy consistency and was found to be highly adhesive to glass surfaces.

A viscous solution of the resin in acetone was spread on two sheets of glass at 30-40°C. with a spatula. The two sheets were then placed together, so that the coated surfaces faced each other.

After standing for several days the glass sheets were firmly held together.

Picric acid was found to be exceedingly soluble in N.G.F.P. In a viscous solution of N.G.F.P. in acetone, picric acid was dissolved up to 50% by weight of cured N.G.F.P. The solution was extremely sticky, and cured to a clear brittle resin at 100°C. Examination under a microscope showed no crystals of picric acid. This phenomenon was taken as evidence for the tendency of picric acid to enter into a resinous complex.

Moldability

Cured and pulverized N.G.F.P. was found to be a suitable powder for molding operations. This material was extruded through a 3/16 in. orifice at a temperature of 140°C. and a pressure of 2,000 lb./sq.in. to give cords of good burning qualities. The cords were smooth and hard, of uniform diameter and exhibited an inherent streaking effect. Streaking was also observed when highly concentrated N.G.F.P. solutions were stirred with a glass-rod. This phenomenon was interesting to note since Freundlich pointed out that plastic masses composed of decidedly non-spherically shaped particles display characteristic streaks on stirring, showing a persistent layering effect.

Cured and pulverized N.G.F.P. was also press-molded into buttons both in the cold and at elevated temperatures, depending on the degree of curing. Thus, the resin cured to a "softening"-point of 80-85°C. was molded at room-temperature and 3,000 lb./sq.in. whereas the resin cured to its maximum "softening"-point of 150-155°C. was molded at 3,000 lb./sq.in.; but a molding temperature

of 130°C. was required.

A heavy-bodied solution of N.G.F.P. in acetone was cast into small glass cups. The casting was allowed to cure at 50°C. for 3 days, at which time a solid, brittle, clear thermoplastic resin was obtained, somewhat resembling rosin. The molded product, when struck with a hammer gave a conchoidal fracture.

Colloidal Properties

The remainder of this section will be devoted to a qualitative description of some of the colloidal phenomena observed during experimental work on N.G.F.P. which showed that this material was a lyophilic-colloidal system.

The viscosity of a 5% solution of N.G.F.P. in acetone was much greater than that of the pure solvent. The acetone of such a sol was evaporated slowly at 30°C. As the system became increasingly poor in external phase, the viscosity increased until finally the sol became so heavy-bodied that it set to a plastogel.

A small parallel beam of sunlight was passed through a 5% solution of N.G.F.P. in acetone. At first a very indistinct Tyndall effect was observed; but after a small quantity of ether (in which N.G.F.P. is insoluble) was added carefully, so that the stability of the sol was not disturbed, the Tyndall effect became quite pronounced and the sol turned bluish. The increase in the clarity of the Tyndall effect is no doubt due to a partial "de-acetonation" of the lyophilic colloid by ether.

This demonstration of the colloidal nature of N.G.F.P. indicates that the polyreaction between nitroguanidine and formal-

dehyde had proceeded to a degree where large molecules were formed, and a high molecular weight must be assumed.

At this point it should be recalled that during the N.G.F.P. preparation the reaction mixture became "moderately" viscous. This must have been due to the growth of molecules to colloidal dimensions and subsequent solvation of the macromolecules by the reaction medium. Thus it may be said, that at reaction temperature (96°C.) N.G.F.P. was a hydrophilic colloid, soluble in the aqueous medium. On cooling, however, the hydrophile separated as a plastogel.

This gel was heated in a distilling flask at 100°C. and water and excess formaldehyde driven off over a period of 10 hours, during which the plastogel was converted to a thermoplastic resin or xerogel of "softening"-point 150-155°C. The plastogel obtained by concentration of an N.G.F.P. - acetone sol was similarly cured at 100°C. to a thermoplastic resin or xerogel of "softening"-point 150-155°C.

The N.G.F.P. plastogel was found to be readily dispersed in acetone or nitromethane at room-temperature by stirring with a glass-rod; whereas the xerogel was dispersed with difficulty, requiring several hours of reflux. In concentrated hydrochloric acid, however, both types of gel were dispersed with ease at room-temperature by stirring.

The N.G.F.P. plastogel was found to flow at a temperature of 25-30°C. and gel again on cooling below this range. The xerogel flowed at a temperature of 150-155°C. and gelled again when cooled below this range. The "melted" gels in both cases were

highly viscous. Accordingly they may be termed heat-reversible viscogels.

Viscous N.G.F.P. - acetone sols exhibited the phenomenon known as rheopexy since gelation was greatly hastened by slow but pronounced elliptical stirring. The gels formed in this way exhibited a silky, streaking effect which was no doubt due to the parallel alignment of N.G.F.P. chain molecules.

A plastogel was separated by the careful addition of 100 ml. ether to 100 ml. 10% solution of N.G.F.P. in acetone. When the ether was added rapidly an amorphous powder precipitated which could be redispersed in acetone. The action of the ether in producing this effect was probably due to the desolvation of the colloidal particles since N.G.F.P. is insoluble in ether.

A 10-g. sample of the plastogel formed by the addition of ether to an N.G.F.P. - acetone sol was allowed to stand for 48 hours in a stoppered test-tube. After this time the gel had shrunk considerably and had liberated an acetone - ether solution which had constituted part of the external phase.

Swelling was observed when acetone, nitromethane or concentrated hydrochloric acid was mixed with the N.G.F.P. plastogel , although it was more pronounced and rapid when concentrated hydrochloric acid was used. Swelling and solution of the xerogel was slow when acetone or nitromethane was used. However, the xerogel swelled and dispersed rapidly in concentrated hydrochloric acid.

The Chemistry of N.G.F.P. Formation

It is apparent in the reaction between nitroguanidine and formaldehyde that there has been a transformation of a low molecular weight compound into a complex derivative of high molecular weight.

In any polyreaction, from compounds of low molecular weight to high polymers there is a continuous transition through compounds of medium size, and a regular change occurs in the various physical properties as the molecular weight increases. The following section contains a study of such a transition in the N.G.F.P. polyreaction.

The complexity surrounding the determination of accurate figures for molecular weights of high polymers was mentioned in a previous section. Although methods are available for their determination, such a specific study was considered unnecessary for the purposes of this research. Instead, the reaction product was divided into three fractions "A", "B" and "C" of decreasing average molecular weight. The rate of formation of these fractions was studied relative to one another, using various physical properties for their characterization.

Seven N.G.F.P. reactions were carried out according to the following scheme.

A mixture of 104 g. (1 mole) nitroguanidine, 246 g. 37% formalin (3 moles formaldehyde) and 82 g. water was introduced into a one-litre three-necked-flask equipped with a mercury-seal-stirrer, a reflux condenser and a thermometer. All the joints were ground-glass. The reaction mixture was refluxed at 96°C.

for 25 minutes, at which time a water-clear solution of monomethylolnitroguanidine was obtained. At this point 57.3 g. (0.25 mole) picric acid were introduced and the mixture refluxed for a further period:

Run No. 1 was refluxed for 15 minutes;

Run No. 2 was refluxed for 30 minutes;

Run No. 3 was refluxed for 45 minutes;

Run No. 4 was refluxed for 60 minutes;

Run No. 5 was refluxed for 90 minutes;

Run No. 6 was refluxed for 120 minutes;

Run No. 7 was refluxed for 180 minutes.

At the conclusion of each of these periods, the hot, clear reaction solution was filtered to remove any impurity. The viscosity and hence the degree of polymerization of these solutions increased from Run No. 1 to Run No. 7. The filtrates were placed in 500-ml. stoppered flasks and allowed to cool to 15°C.

Fractionation of the reaction product in each case was carried out in the following manner.

On cooling, the reaction solutions spontaneously deposited a plastogel from which the supernatant liquid was decanted and set aside for further fractionation. A certain quantity of picric acid was precipitated along with this plastogel which was removed by reprecipitation of the gel. Accordingly, ether was carefully added to a dispersion of the gel in acetone and the plastogel "A" reprecipitated leaving the picric acid in solution. Evaporation of the solution yielded the picric acid.

The original supernatant liquid was fractionated according to the following procedure.

Cold water was carefully added, with stirring, until a subsequent precipitation was complete. The quantity of water thus required was recorded. The mixture, composed of a voluminous milky precipitate suspended in a liquid medium, was placed in an ice box at 15°C. and allowed to stand. After 12 hours a clear liquid was decanted from a plastogel "B". This supernatant liquid was evaporated in a vacuum apparatus over a steam-cone, to a viscous syrup which set to a plastogel on cooling. This plastogel "C" was redeposited from an acetone dispersion by the addition of ether.

It will be observed that, the order of solubility of the three fractions "A", "B" and "C" decreases from "C" to "A"; fraction "A" was spontaneously deposited when the reaction solution was cooled; fraction "B" was deposited upon the addition of water to the supernatant liquid, leaving the most soluble fraction "C" in solution.

It was assumed that the three polymeric fractions consisted of chain molecules. This assumption was considered to be justified however, in view of certain properties already observed which are characteristic for linear polymers or chain molecules.

Mention has already been made of the solubility dependence of chain molecules on the length of the chain. In brief, the solubility decreases with rise in chain length. Thus the N.G.F.P. homologous series has been separated into three fractions of dif-

ferent <u>average</u> chain length; the average chain length increasing from "C" to "A".

This consideration was supported by other physical properties, namely, viscosity and plasticity.

The viscosity of the "melted" gels markedly increased from "C" to "A". Since viscosity increases with the length of the molecule (113) the degree of polymerization also increases from "C" to "A".

The plasticity (i.e. the ability to retain a shape on deformation) of the gels markedly increased from "C" to "A". Since plasticity increases with the length of the molecule (114) the degree of polymerization also increases from "C" to "A".

For the sake of simplicity the fractions "A", "B" and "C" were considered to be composed of "long", "intermediate", and "short" chain molecules respectively.

Results are given in the following table and graph.

The general nature of the results indicated in Fig. 1 show that a type of consecutive reaction is involved:

Mono-methylolnitroguanidine ⟶ "x" ⟶ "C" ⟶ "B" ⟶ "A"

The significant role of picric acid is demonstrated in the rapid accumulation of "C". Upon the addition of picric acid, mono-methylolnitroguanidine probably disappears almost immediately by transformation into a high concentration of activated molecules, represented by the theoretical curve "x". The formation of these activated molecules gives immediate rise to the rapid

TABLE II

Run No.	Time of Reflux in min.	Yield of "A" in g.	Yield of "B" in g.	Yield of "C" in g.	Vol. of H_2O to ppt. "B" in ml.	Amount of pptd. picric acid in g.
1	15	0	15	111	325	34
2	30	2	28	108	240	25
3	45	5	33	105	165	..
4	60	16	40	93	100	10
5	90	54	34	59	150	3
6	120	96	15	44	225	1
7	180	141	5	9	500	0

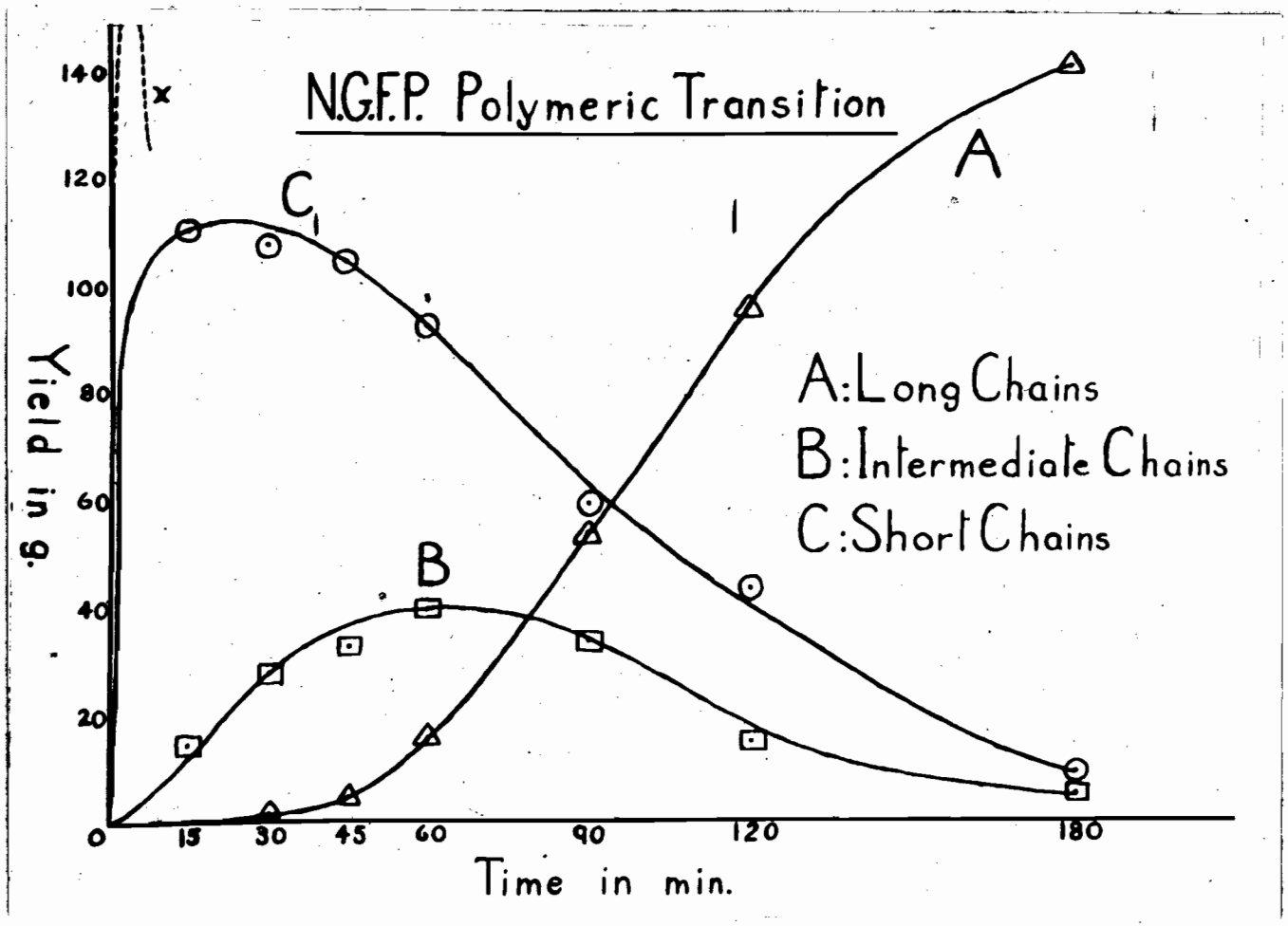

N.G.F.P. Polymeric Transition
Yield in g.
Time in min.
A
C1
B
A: Long Chains
B: Intermediate Chains
C: Short Chains
0
15
30
45
60
90
120
180
20
40
60
80
100
120
140

FIGURE I

accumulation of their product "C" (molecules of "short" chain-length). The amount of "C" increases rapidly, but as it accumulates its disappearance becomes greater and it passes through an early maximum. The amount of "C" then decreases steadily, since it disappears in an exponential manner, irrespective of the fate of its product "B" (molecules of "intermediate" chain-length). The amount of "B" increases at first, and similarly passes through a maximum, then steadily disappears and finally of course approaches zero. As the amount of "B" slowly accumulates, its product "A" (molecules of "long" chain length) slowly begins to form, passing through an induction period corresponding with the maximum concentration of "B". The amount of "A" then steadily accumulates as "B" disappears, until ultimately it approaches its maximum which of course corresponds with the initial concentration of reactant "x".

It must be borne in mind, however, that none of the fractions "A", "B", or "C" is to be considered as being composed of chains of equal length, but rather each fraction is to be viewed as consisting of a continuous transition of chain-lengths in itself. Theoretically, by an exceedingly refined fractionation technique, a complete series of these curves would be obtained, from the disappearance of reactant "x" to the formation of the longest chain.

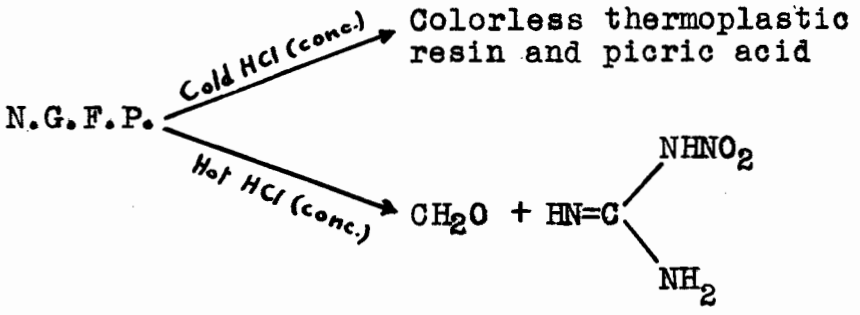
Thus from mono-methylolnitroguanidine to "long"-chain molecules, by a series of consecutive reactions, there is a continuous transition through "short" and "intermediate" chain lengths.

The disappearance of precipitated picric acid from the cooled reaction solution and the high yields of polymer indicated the consumption of the acid. However, the essential role of picric acid must be considered as catalytic since it was found not to enter the basic structure of the polymer chains. The following qualitative analysis of N.G.F.P. was carried out.

A small amount of N.G.F.P. (ca. 10 g.) was dispersed in 50 ml. cold concentrated hydrochloric acid and the dispersion extracted ten times with 75-ml. portions of ether. Evaporation of the ether extract yielded picric acid. Addition of water or ethanol to the remaining hydrochloric acid solution caused the deposition of a colorless gel which cured to a thermoplastic resin softening at 135-140°C.

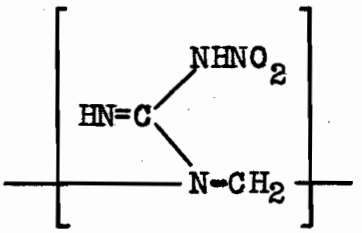
In another experiment the hydrochloric acid solution, remaining after ether extraction of picric acid, was heated to 100°C. and evaporated to small volume over a Bunsen flame. During this procedure formaldehyde was given off and white needles crystallized out which, after recrystallization from water solution, melted at 235°C. A mixed melting-point with nitroguanidine gave no depression.

The results of these experiments may be summarized as follows:



This evidence indicated that the structural units of N.G.F.P. chain molecules were joined by hydrolizable methylene bridges and that picric acid was held to the chain molecules by salt formation.

Cold hydrochloric acid being a stronger acid is apparently capable of releasing the picric acid without decomposing the basic polymeric structure. Hot hydrochloric acid, however, causes hydrolysis of the chain molecules with evolution of formaldehyde and formation of nitroguanidine. Since the transformation to N.G.F.P. chain molecules occurs by the catalytic action of picric acid on mono-methylolnitroguanidine, the most obvious structural unit is methylenenitroguanidine.



Further research showed that a resin was formed when equimolecular quantities of mono-methylolnitroguanidine and picric acid were fused at 100°C.

An intimate mixture of 2.29 g. (0.01 mole) picric acid and 1.34 g. (0.01 mole) mono-methylolnitroguanidine was heated to 100°C. for 10 minutes, during which time water vapour was evolved and collected in a dry-ice bath and a N.G.F.P. resin was formed. At the end of the experiment the weight lost by the mixture in forming the resin corresponded to 0.17 g. (0.0095 mole) water. It thus appeared that one mole of water was eliminated per mole of resin formed and that the picric acid caused the mono-methylol-

guanidine to form a polymer by this loss of water.

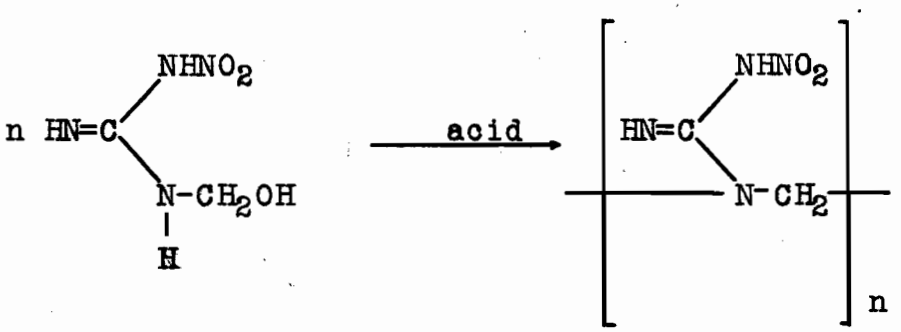
This view was supported by an experiment in which esterification of mono-methylolnitroguanidine was attempted.

A small quantity (13.4 g.; 0.1 mole) mono-methylolnitroguinidine was dissolved in hot, pure acetic acid. Upon the addition of about 28 g. (0.2 mole) benzoyl chloride to the cooled solution, a white crystalline compound precipitated which was filtered off. When ether was added to the filtrate a milky precipitate was formed which settled to form a gel. Recrystallization of the crystalline precipitate from ether solution gave white crystals melting at 121°C. and a mixed melting-point with benzoic acid caused no depression. When benzoyl chloride was added to pure acetic acid no reaction occurred.

From this experiment it is evident that the transition from mono-methylolnitroguanidine to large molecules, as evidenced by the formation of a gel, occurred by the loss of water. This was presumably a result of the catalytic action of acetic acid. Since benzoyl chloride did not hydrolize when added to pure acetic acid, the formation of benzoic acid, upon its addition to a pure acetic acid solution of mono-methylolnitroguanidine, must have occurred by reaction with liberated water.

A similar gel was formed by the addition of ether to a pure acetic acid solution of mono-methylolnitroguanidine whether or not it had previously been treated with acetyl chloride, thus bearing out the contention that the loss of water was occasioned by the catalytic action of acetic acid.

It is evident that the loss of water from mono-methylol-nitroguanidine will give methylenenitroguanidine:



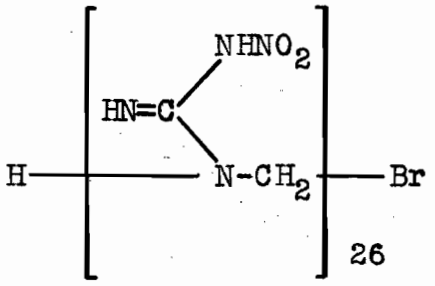
In another experiment 15 g. mono-methylolnitroguanidine were dissolved in 100 ml. 20% bromine solution in glacial acetic acid. Upon the addition of ether a reddish-brown sticky material separated as a gel. After decanting the supernatant liquid, the material was repeatedly washed with glacial acetic acid and ether, but the reddish-brown color persisted. However, the substance was regarded as a polymer containing a large amount of loosely held bromine since on curing to a resin, bromine was continuously evolved and the substance lost most of its color. Further, a white amorphous powder was obtained entirely free of a bromine odour after several depositions of the material from acetone solution by the rapid addition of ether.

The problem of purifying polymeric substances prepared in the above ways is a difficult one and although scrupulous purification of these substances is not possible by ordinary means, elementary analyses of the amorphous powder, obtained in the previous experiment, gave results which no basic structural unit other than methylenenitroguanidine approached:

Calcd. for: $H-\left[C_2H_4O_2N_4\right]_{26}-Br$: C, 20.14; H, 3.39; N, 47.01; Br, 2.58%

Found: C, 19.14, 19.35; H, 3.76, 3.67; N, 48.82, 48.45; Br. 2.58, 2.58%. (a)

Assuming 100% accuracy for the bromine analyses, the following structure best fits these figures:



On the basis of the preceding experiments, the recurring unit in N.G.F.P. chain molecules was postulated as methylene-nitroguanidine. This postulate is in complete accord with the property of methylolamines in general to form methyleneamines by loss of water in the formation of higher products.

Applications of N.G.F.P.

N.G.F.P. Burning Mixtures

The Standard Composition, used in the 17 pounder A.P. shell at Cherrier, Que., was found to be inadequate for use in the 40-mm. A.A. shell because a longer burning-time (ca. 15 secs.) was

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(a) The carbon analyses were carried out at the Division of Industrial and Cellulose Chemistry, McGill University, Pulp and Paper Research Institute of Canada, Montreal.

The nitrogen and bromine analyses were carried out in the Microanalytical Laboratories of the National Research Council, Ottawa.

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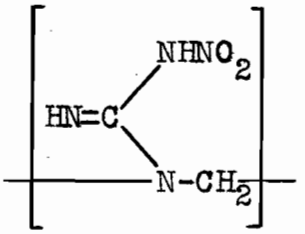
required in these shells, and it could not be obtained without excessive quantities of the Standard Composition. Thus a new tracer composition was desired which would give the longer burning-time with the same luminosity and yet occupy a volume no larger than the three 1.3-gram pellets then in use.

Experiments were conducted, adding various oxygen carriers to samples of cured N.G.F.P. in order to improve its burning qualities.

If the repeating unit in N.G.F.P. is indeed the fragment postulated:



then for complete combustion to carbon dioxide, water and nitrogen, 116 g. polymer would require 96 g. oxygen, of which 32 g. is already available; or 100 parts of polymer would require 55.2 parts added oxygen. In this speculative calculation, the picric acid has been omitted.

Mixtures of N.G.F.P. with various amounts of potassium chlorate, calcium nitrate and potassium nitrate were prepared and burned in an open dish, as loose powders, with the results listed in Table III.

TABLE III

Oxygen Carrier	Amount in g. N.G.F.P.	Amount in g. Carrier	Burning Time in seconds	Remarks
$KClO_3$	2.5	2.5	0.5	Extremely brilliant flame; cloud of white smoke.
$Ca(ONO_2)_2$	2.5	2.5	15.6	Hot orange-red flame.
$KONO_2$	2.5	2.5	30.0	Sputtering flame and difficult ignition.

Thus it would seem that control of the burning-rate can be achieved by choosing a suitable oxygen carrier.

Since greater visibility is imparted to burning-mixtures by the addition of compounds which give a colored flame, such as barium nitrate in aircraft signals which imparts a green color to the flame, and strontium nitrate which is generally used in tracer compositions to give a red trace (115), samples of a mixture containing N.G.F.P., potassium chlorate and strontium nitrate were made and pelleted at Canadian Car Munitions, Cherrier, Que. It was found that the burning-time was constant and it was suggested that N.G.F.P. might be of use in a tracer composition.

Further mixtures were investigated in the laboratory substituting potassium perchlorate for potassium chlorate and adding magnesium powder to increase the brilliance of the flame. The following proportions were found to give a red flame with

high luminosity, when burned as a loose powder in the laboratory: 5.8 parts N.G.F.P., 6.8 parts $KClO_4$, 2.5 parts Mg powder and 4.2 parts $Sr(NO_3)_2$.

In agreement with Marshall (116) it has been found that addition to these mixtures of a small amount of calomel (1 g. calomel to 20-g. mixture) both decreases the rate of burning and enhances the intensity of flame color. The latter is probably due to formation of strontium chloride which has a red spectrum.

Ten mixtures containing N.G.F.P. and various oxygen carriers were made up, pelleted and compared with respect to (a) burning time and (b) luminosity, against the Standard Tracer Composition used in the 17 pounder A.P. shell at Cherrier, Que.

The mixtures pelleted well and were pressed into 17 pounder A.P. shells and sealed against moisture without any trouble. The burning-times were good and it can be seen from the results arranged in Table IV that a mixture burning for 15 sec. was obtained. However, the luminosity results were uniformly and exceptionally low despite the fact that to the naked eye the flames produced appeared to be as brilliant as those obtained from the Standard Composition. Relative luminosity was measured using a standard light-meter containing a green filter, and, since the mixtures investigated burn with an intense crimson flame, it can be presumed that much of the light was absorbed before entering the instrument. Standard Tracer Composition burns mostly with a white light and therefore

TABLE IV

Mixture No.	N.G.F.P. in %	$Sr(NO_3)_2$ in %	$BA(NO_3)_2$ in %	$KClO_4$ in %	Mg in %	HgCl in %	Burning Time in sec.	Luminosity
1	28.4	51.6	0	0	5.0	15.0	11	2
2	32.2	44.6	3.2	0	0	20.0	14	6
3	20.2	44.0	0	0	10.8	25.0	15	8
4	24.4	45.6	0	0	5.0	25.0	19	4
5	31.2	45.0	0	5.4	3.4	15.0	21	2
6	35.8	36.6	0	13.6	0	15.0	31	1
7	35.2	41.6	0	8.2	0	15.0	33	1
8	33.8	41.6	9.6	0	0	15.0	36	1
9	31.8	29.6	0	13.6	0	25.0	39	1
10	31.2	35.6	0	8.2	0	25.0	40	1
			Standard Tracer Composition				8	70

the basis of comparison is invalid. The presence of the green filter does not seem to be necessary and this point was referred to the Ammunition Filling Division of the Department of Munitions and Supplies.

All the N.G.F.P. mixtures were balanced theoretically with respect to oxygen. Calomel was added both to increase the burning-time and to enhance the intensity of the red color.

Following these trials, five more mixtures based on N.G.F.P. were worked out. Ten-gram samples of these new tracer compositions were ignited electrically as a loose powder, and the burning-time and luminosity recorded in the laboratory using a white-light meter (i.e. without a green filter as previously discussed).

The Standard Tracer Composition was used as a reference and the results assembled in Table V clearly show that a longer burning-time can be obtained without decreasing the luminosity.

These experimental compositions were pelleted and tested for burning-time and luminosity in 17 pounder A.P. shells at Cherrier, Que. The light-meter used to determine luminosity contained no green filter and the compositions were compared with Standard Tracer Composition.

From the results given in Table VI it is evident that the burning rates at high density are much slower than those obtained at low density (i.e., in powdered form). The discrepancy between these relative luminosities and those in Table V were not readily accounted for until it was learned from the National

TABLE V

Sample No.	Asphalt in %	N.G.F.P. in %	$Sr(NO_3)_2$ in %	Mg in %	Al in %	HgCl in %	Burning Time in sec.	Luminosity
Standard	9.1	0	45.5	22.7	0	22.7	5.0	15.0
1	0	9.1	45.5	22.7	0	22.7	6.0	15.0
2	0	10.2	46.6	18.2	0	25.0	6.0	16.0
3	0	10.2	48.2	9.1	7.5	25.0	8.0	15.0
4	0	13.5	42.3	6.0	4.9	33.3	11.0	12.0
5	0	8.1	49.0	9.1	8.8	25.0	12.0	14.0

Defense Research Committee of the Office of Scientific Research and Development (117) that U.S. Army surveillance tests found that raw powdered magnesium corrodes very rapidly in such mixtures containing nitrates and on exposure to atmospheric humidity.

The magnesium used in Standard Tracer Composition was precoated with linseed oil; whereas the magnesium used in the preparation of N.G.F.P. tracer compositions was untreated.

The N.G.F.P. tracer compositions listed in Table V were tested immediately after preparation, and those listed below in Table VI were not pelleted and sealed against moisture in the 17 pounder A.P. shell until two weeks after preparation. Thus the difference in luminosities can be presumed to be partially due to deterioration of magnesium. However, it appears that magnesium is the critical component in the production of luminosity as tested by a white-light meter. The N.G.F.P. tracer compositions produced a much more intense red flame and much less luminescent white light than the Standard Tracer Composition. This view was substantiated by a report from the Explosives Research Laboratory (118) which states that magnesium is less effective in producing a red color than other reducing agents because of the masking effect of the white luminescence of burning magnesium.

An increase in the proportion of magnesium seems to decrease the burning-time and substitution of aluminium for magnesium seems to give much lower intensities.

TABLE VI

Sample No.	Asphalt in %	N.G.F.P. in %	$Sr(NO_3)_2$ in %	Mg in %	Al in %	HgCl in %	Burning Time in sec.	Luminosity
1	0	9.1	45.5	22.7	0	22.7	11.0	9.0
Check							10.2	9.0
2	0	10.2	45.6	18.2	0	25.0	14.0	6.0
Check							16.0	6.0
3	0	10.2	48.2	9.1	7.5	25.0	17.8	1.8
Check							18.0	1.8
4	0	13.5	42.3	6.0	4.9	33.3	26.0	0.6
Check							26.0	0.6
5	0	8.1	49.0	9.1	8.8	25.0	19.0	3.0
Check							19.6	3.0
Standard	9.1	0	45.5	22.7	0	22.7	7	12.0
Check							8	15.0

Thus it appears that these N.G.F.P. tracer compositions have a greater burning-time, a greater intensity of red light, but less luminescent white light.

It should be pointed out that the figures given in these tables represent static burning-times, that is, the shells were not spun along their axis with a blast of air blow past them to simulate ballistic tests.

High Explosive Phlegmatization and Fillings Using N.G.F.P.

It was found that R.D.X. could be dissolved in N.G.F.P. by solution in acetone or nitromethane followed by evaporation of the solvent. Using the method of preparation described below, a resin containing 14.2% R.D.X. was made. This material was named N.G.R.

To 100 g. 30% N.G.F.P. - acetone solution, in a 250-ml. beaker, R.D.X. was added in small quantities, allowing each portion to dissolve after each addition, until a total of 5 g. was added. It was necessary on occasion to break up conglomerates with a stirring-rod.

After the R.D.X. was dissolved, the beaker was covered with a watch-glass and warmed on the steam-cone for one hour, after which the watch-glass was removed and the acetone evaporated off. Finally the syrup was heated until it set to form a plastogel on cooling.

On further heating a cured resin was obtained which gave a brittle material, suitable for grinding.

No crystals were detected either in the resin or in the ground molding powder, even when these were cooled to -60°C. in

a Dewar-flask.

The calorific value of N.G.R. was determined in a closed bomb by Defence Industries Ltd. at Nobel, Ont. and the values of 515 and 514 cal./g. were obtained.

It was proposed to name other N.G.F.P.-R.D.X. preparations by enclosing the percentage of R.D.X. in a bracket following the letters N.G.R. eg N.G.R.(14).

N.G.R.(14) was tested by M.C. Fletcher in the Explosives Laboratory of the Department of Mines and Resources, Ottawa. It was found to be less sensitive than T.N.T. When fired in the ballistic mortar an average value of 0.86 x T.N.T. was obtained. There was no evidence of indent in the steel-plate-test.

N.G.R.(14) was pressed into time-ring-fuses by Dr. Wright at Toronto, and the material was found to burn poorly at high density.

It was found that the R.D.X. content of N.G.R. could be determined quantitatively by fuming-off the material with 70% nitric acid.

A sample of N.G.R.(15) was examined microscopically by Dr. W.C. McCrone Jr. and the presence of a few R.D.X. crystals was demonstrated by fusion analysis.

Samples of N.G.R. containing up to 90% R.D.X. were prepared. In all cases the syrup increased steadily in viscosity, during curing, until a yellow, brittle resin was obtained which could be ground.

Observations under the polarized microscope, kindly carried out by Professor Fitz Osborne, of the Department of Geology,

McGill University, have shown that the higher the R.D.X. content of N.G.R., the less dispersion of R.D.X. throughout the polymer or, the higher the R.D.X. content, the higher the amount of anisotropic material embedded as minute R.D.X. crystals throughout the polymer. Professor Osborne estimated the amount of crystalline R.D.X. in a sample of N.G.R.(30) to be between 4 and 12%.

A wide range of N.G.R. samples was sent to Canadian Industries Ltd., McMasterville and the University of Toronto for sensitivity determinations and to the Explosives Testing Laboratory, Ottawa, for sensitivity and explosive force measurements. Samples were prepared with British R.D.X. and R.D.X.(B) coarse, fine, and recrystallized from acetone. Absolute agreement was not obtained throughout but in general terms it can be said that (a) N.G.R. is less sensitive than R.D.X., (b) as the R.D.X. content of N.G.R. increases, the sensitivity also increases, (c)as the R.D.X. content of N.G.R. increases, the explosive force also increases. These results are recorded in Table VII.

Friction Impact Sensitivity Determinations were carried out at the Explosives Testing Laboratory, Ottawa. These tests were run using a serrated anvil and a 6-pound shell which had the pointed nose rounded off, leaving a net weight of 5 lb. 11 oz. The angle of slide was 30° and the sample was covered with a small piece of fine sandpaper before firing. The results are given in Table VIII.

TABLE VII

Material	Remarks	Sensitivity: McMaster-ville 2kg. weight 50% height in cm.	Sensitivity: Toronto 50% height in cm.	Sensitivity: Ottawa 50% height in cm.	Ballistic Mortar: T.N.T. 1	Ballistic Mortar: T.N.T. 1	Ballistic Mortar: Remarks
N.G.R.(10)	R.D.X.(B)			66	0.88	0.14	Incomplete detona-
N.G.R.(15)	R.D.X.(B)			58	1.00	0.14	tion
N.G.R.(20)	R.D.X.(B)			60	0.96	0.38	do
N.G.R.(25)	R.D.X.(B)			48	1.21	0.81	
N.G.R.(30)	R.D.X.(B)			50	1.16	0.87	
N.G.R.(50)	R.D.X. (fine)	75	200	51	1.1		
N.G.R.(50)	R.D.X. (coarse)	88	160	34	1.8	1.15	
N.G.R.(50)	R.D.X. (recrys.)	85	185	22	2.7	1.16	
N.G.R.(50)	British	88	180	34	1.8		No. 6 cap used
N.G.R.(50)	plus KNO_3	73	150	40	1.5	1.03	
N.G.R.(75)	R.D.X.(B)	60	175	24	2.5	1.38	throughout
N.G.R.(80)	R.D.X.	60	210	38	1.6	1.41	
N.G.R.(90)	British	65	150	26	2.3	1.43	
R.D.X.	British		100	32	1.9		
R.D.X.(B)				36	1.7		

TABLE VIII

McGill Material				Friction Impact cm. Height		
N.G.R.(50)	R.D.X.	fine		135	NEG	(Max. Ht.)
"	"	"	coarse	135	"	
"	"	"	recryst.	135	"	
"	"	"	British	135	"	
"	"	plus KNO_3		75	"	Very positive
N.G.R.(75)	R.D.X.(B)			60	cm.	Pos. (minimum)
N.G.R.(80)	"			65	"	" "
N.G.R.(90)	British			55	"	" "
R.D.X.	"			42	"	" -
R.D.X.(B)	-			40	"	-

At Toronto, Friction Impact Sensitivity determinations were also carried out. In these determinations a 6-pound projectile, a smooth anvil and an angle of slant 30° was used; under these conditions British R.D.X. shoots at 200 cm. No detonations with any sample of N.G.R. was obtained.

The McMasterville report reads in part ..."These materials are all less sensitive than tetryl, but more sensitive than T.N.T.".

Thus a definite phlegmatization of R.D.X. by N.G.F.P. had been obtained.

Several P.I.A.T. bombs were filled with N.G.R.(90). The filling operation was accomplished smoothly, after which the bombs were easily assembled. The preparation of N.G.R.(90)-bomb-filling and the method of filling were as follows.

To 1,000 g. 5% N.G.F.P. - acetone solution, in a steam-

jacketed 2,000-ml aluminium beaker, R.D.X. was added in small quantities, with stirring, until a total of 450 g. was added. The acetone was evaporated slowly while the mixture was stirred, until a heavy-bodied plastic mass was obtained, which became hard on cooling.

The warm plastic N.G.R. was ladled into the cup of the P.I.A.T. bomb; the Munroe cone was inserted and pressed into the filling and the bomb was sealed.

Information was received that, since the P.I.A.T. bomb functions on the Munroe principle, it was necessary for the filling to closely adhere to the cone and walls for its successful operation.

A split P.I.A.T. bomb was filled in the above manner and opened 48 hours later. The N.G.R.(90) casting was smooth, hard, and well formed. There was no evidence of fissures or cracks, however, the casting had shrunk about 0.05 cm. from the walls of the bomb, so that by inverting the bomb, the smooth casting slid out. This defect could not be overcome by this method of filling due to the continued gelation and consequent shrinkage of the N.G.F.P. in N.G.R. after the bomb was filled.

Since the N.G.R.(90) castings were of a good quality they were successfully cemented in the bomb using a rubber adhesive. It was therefore suggested that a suitable phlegmatized R.D.X. P.I.A.T. bomb filling would be obtained by precasting N.G.R.(90) in P.I.A.T. molds and cementing the cured casting in the bomb.

A similar moldable product was obtained, if instead of

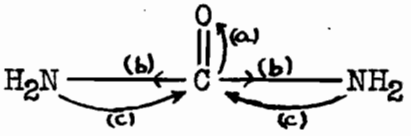
evaporating the acetone from the N.G.R.(90) preparation, it was removed by pouring the mixture into cold water. The N.G.R. separated as a heavy-bodied plastic mass from which the supernatant liquid was decanted. The product contained about 6% by weight of water as determined by loss of weight on drying, and could be worked in the hands or pressed into shape while warm and cured at 50°C. for 5 hours to a hard, solid mass.

DISCUSSION

A Theoretical Consideration of Activation Effects in the Urea and the Nitroguanidine Molecule

It is well known that a molecule must be activated before it can react. This activation involves a shift of electrons before reaction, that is, an increase in electron density occurs in one portion of the molecule and a corresponding decrease occurs in another portion of the molecule.

The urea molecule consists of two amino-groups attached to a carbonyl-group:



The carbonyl-group is permanently polarized due to a "positive" electromeric effect (a) and is thus a potential electron-acceptor center.

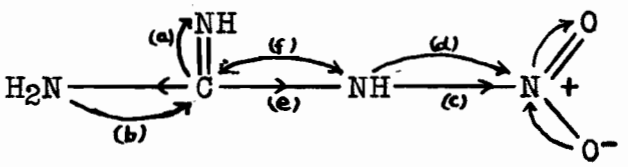
In the bonds uniting the carbonyl-group to the amino-groups, there are two electron displacement effects operating, one against the other; namely: a "positive" inductive effect (b) and a "negative" electromeric effect (c).

The urea molecule is therefore internally compensated. The acceptor center, i.e., the carbonyl-group, greatly enhances the "negative" electromeric effects (c) and the "positive" inductive effects (b) become negligible. Thus the electromeric shift of

electrons from the carbon- to the oxygen-atom (a) is compensated for by the electromeric shift of electrons from the amino-groups, thereby de-activating the carbonyl-group and activating the two amino-groups.

The validity of this reasoning is seen in the formation of di-methylolurea, in the urea-formaldehyde reaction since the formation of di-methylolurea implies that both amino-groups are active.

The electronic effects operating in the nitroguanidine molecule are more complex, due particularly to the presence of a nitro-group:



The imino-group in nitroguanidine like the carbonyl-group in urea is permanently polarized, and again due to internal compensation (a) and (b), the amino-group becomes activated. Although the power of the imino-group to withdraw electrons from the amino-group is less than that of a carbonyl-group, the highly electronegative character of the nitro-group will compensate for this weakness.

The nitro-group is itself an internally compensated system, and the incipient positive charge on the nitrogen atom will establish a strong "positive" inductive effect (c), which augmented by the "positive" electromeric effect (d) will result in a decreased electron density on the nitroamino-nitrogen atom. This decreased

electron density, supplemented by the "positive" inductive effect (e) will be sufficient to reverse the normal "negative" electromeric effect and cause a "positive" electromeric electron displacement (f) and an over-all withdrawal of electrons from the carbon-atom and hence from the amino-group.

Both the imino-group and the nitroamino-group will tend to become de-activated by their withdrawal of electrons from the amino-group and the amino-group will become activated.

This reasoning is consistent with the fact that a substituent always enters the non-nitrated amino-group in the formation of substituted nitroguanidine (119,120) and by the formation of mono-methylolnitroguanidine in the nitroguanidine - formaldehyde reaction, even when an excess of four moles of formaldehyde is present.

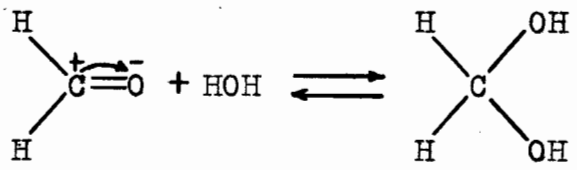
A Discussion of the Mechanisms Involved in the N.G.F.P. Polyreaction

Formaldehyde is usually considered to react in aqueous solution as methylene glycol: $HO-CH_2-OH$ (121). However, since formaldehyde can form normal carbonyl reaction products (122, 123,124) it would appear that it contains at least a potential reactive carbonyl-group. Further, formaldehyde can be replaced by other aldehydes such as acetaldehyde (125), furfuraldehyde (126), aldol (127), and benzaldehyde (128) or certain ketones (129) in the formation of urea-formaldehyde resinous condensation products.

In view of these facts, the carbonyl-group will be considered to be the active component of formaldehyde in these polyreactions.

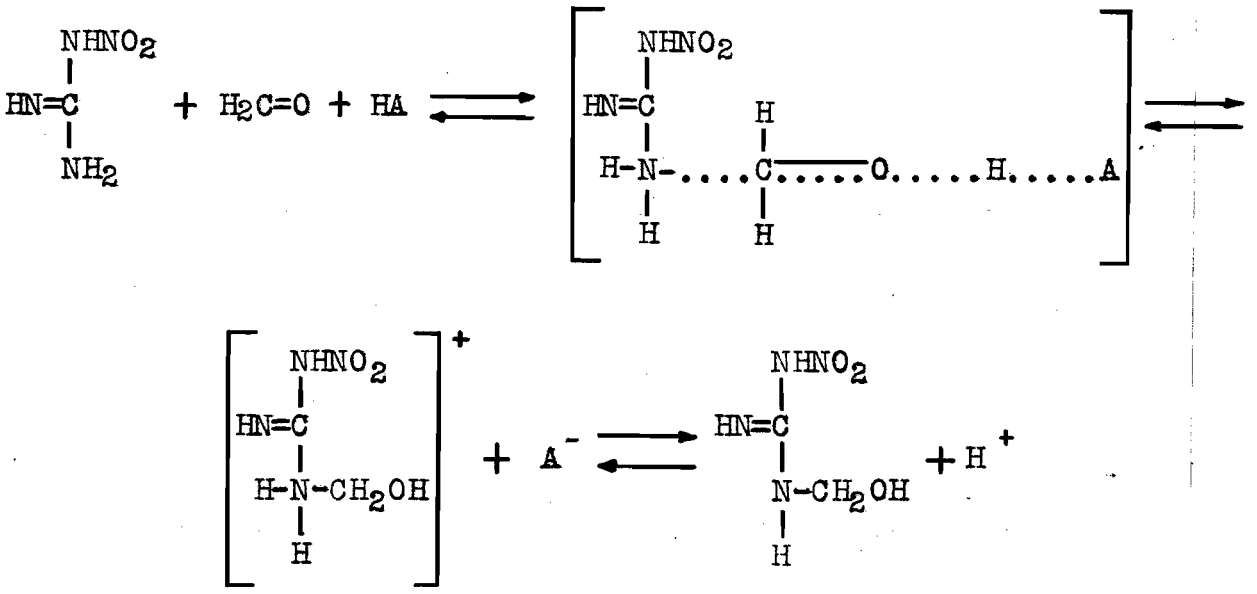
It is known that the electrophilic carbonyl-double-bond will add such substances as water, alcohols and amines reversibly, and its high degree of activity is considered to be due to its permanent polarization.

Since addition reactions involving the carbonyl-double-bond are characteristically reversible, the formation of methylene glycol can be explained as a reversible addition reaction of water to the carbonyl bond of formaldehyde; for example



The addition of amines to the carbonyl-double-bond is also a freely reversible reaction and is subject to acid catalysis. Since the carbon-nitrogen linkage in mono-methylolnitroguanidine is formed by an electron pair contributed by the nitroguanidine amino group, the catalysis must depend upon an attack of the acid on the carbonyl compound. Such an attack will decrease the electron density on the carbonyl-carbon which will favour the formation of the carbon-nitrogen bond; an attack on the amino-group of nitroguanidine would decrease the electron density on the nitrogen which would be unfavourable to reaction.

The formation of mono-methylolnitroguanidine may be considered to proceed according to the following addition mechanism at an acid pH of 3.6:



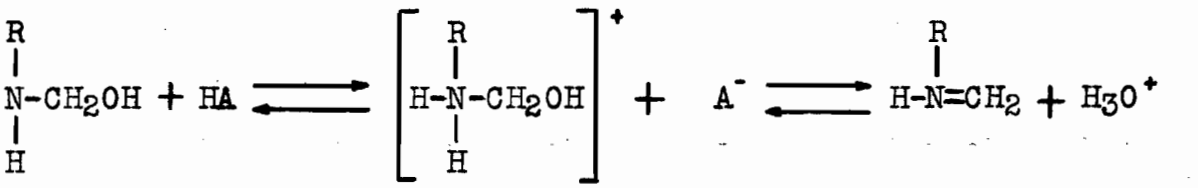
This mechanism would explain the necessity for the presence of an excess of formaldehyde in order to isolate the addition product. The presence of two moles of formaldehyde per mole of nitroguanidine will shift this equilibrium sufficiently to the right to permit this operation. In warm water, however, the equilibrium moves far to the left and the mono-methylol compound decomposes; formaldehyde is evolved and nitroguanidine is recovered.

In the preparation of N.G.F.P., the higher acid concentration, obtained by the addition of picric acid to the hot reaction solution containing mono-methylolnitroguanidine, resulted in the transformation of mono-methylolnitroguanidine to a polymer. A similar transformation was observed by solution of mono-methylolnitroguanidine in pure acetic acid. It was further demonstrated that this polyreaction was accompanied by the loss of water and that the polymeric structural unit was probably methylenenitroguanidine.

That the N.G.F.P. polymer is composed of chain molecules there can be little doubt since the characteristics of linear polymers were evidenced by such properties as thermoplasticity and unlimited swelling in suitable solvents, as well as other colloidal phenomena. Further, it is reasonable to regard mono-methylolnitroguanidine as a bi-functional molecule which could lead only to chain molecules.

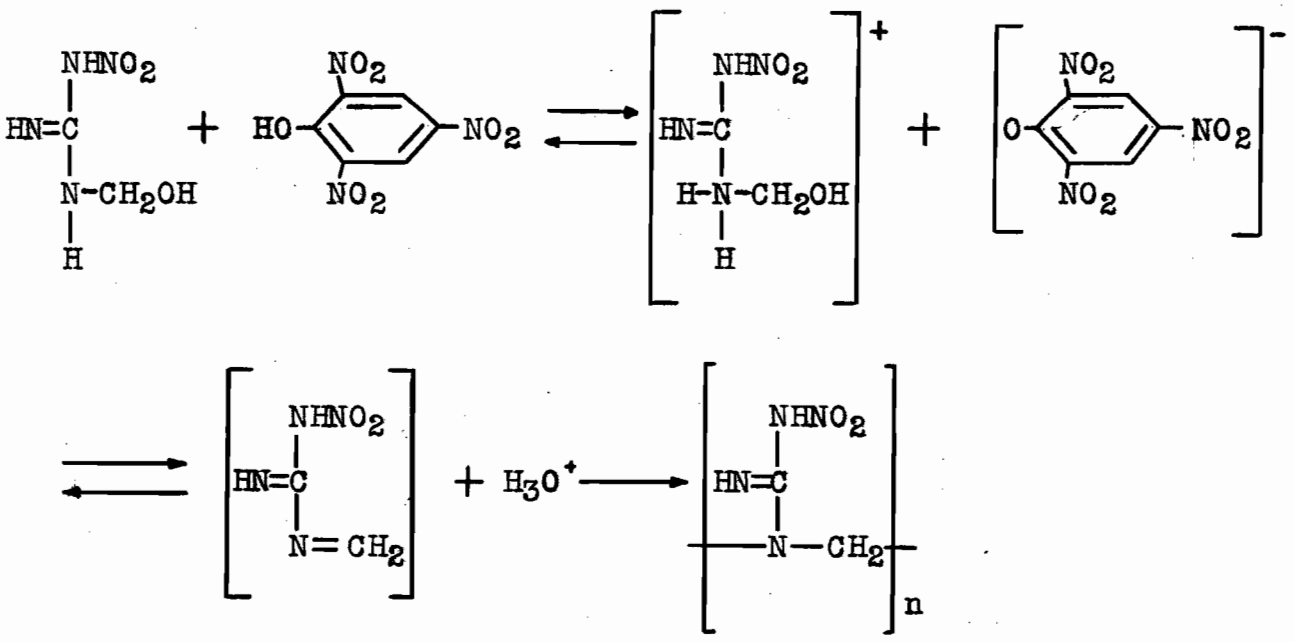
The rate study of N.G.F.P. formation indicated that upon the addition of picric acid, the mono-methylolnitroguanidine in the reaction solution, almost immediately disappeared with the formation of a polymerization factor which rapidly formed a high concentration of "short" chain molecules. The data from this study further demonstrated that the reaction proceeded by a series of consecutive reactions by which "long" chain molecules were formed.

It is well known that the kinetics are often complicated in many reactions involving the addition of amines to carbonyl compounds, because water may be eliminated and the product stabilized in another manner. Further the elimination of water from such addition products is known to be rapid. This elimination of water is pictured as occurring in the following manner:



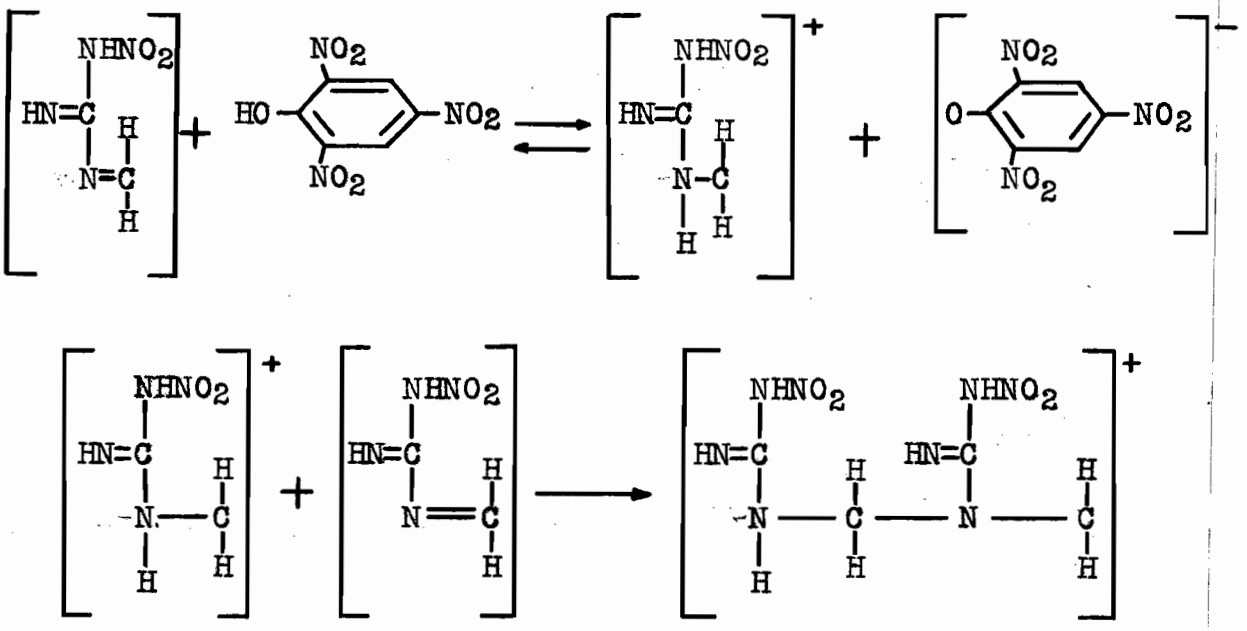
From the known facts regarding the N.G.F.P. reaction it is reasonable to presume that upon the addition of picric acid to

the reaction solution, water is eliminated and methylenenitroguanidine formed. Such an unsaturated molecule is a potential polymerization factor which may stabilize itself by addition polymerization. This reasoning is in complete accord with the known properties of unstable methylol-amines. The mechanism may be considered to be the following:

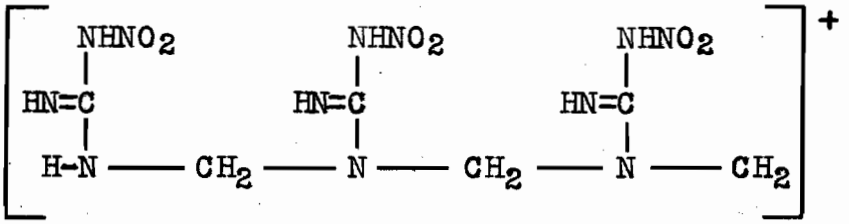


The actual polymerization reaction is regarded as proceeding by an ionic mechanism by acid catalysis similar to the acid catalysed carbonium ion mechanism for the polymerization of olefins (130,131,132).

The mechanism postulated for the polymerization of methylenenitroguanidine is as follows: picric acid attacks a molecule of methylenenitroguanidine to form methylenenitroguanidiniumpicrate, A. The methylenenitroguanidinium ion then reacts with a molecule of methylenenitroguanidine to form B. Thus:



The product, B, is still an ion; if it further reacts with another methylenenitroguanidine molecule to form C, the system is well on its way toward long-chain polymerization.



Thus by a series of consecutive reactions there is a continuous transition from methylenenitroguanidine through "short" and "intermediate" chains to "long"-chain molecules.

As polymerization proceeds, chain molecules are formed which display the properties of internal-phase particles of a lyophilic colloid. The colloidal particles thus formed are solvated, with the reaction-medium at reaction-temperature

(96°C.) either as molecules or as micelles. When "long" chains are formed they are deposited, on cooling, as a plastogel which can be converted to an xerogel or resin of thermal "softening"-point 150°-155°C. by drying (curing).

The color of the scattered light in the Tyndall experiment on an N.G.F.P. sol was seen to be predominantly blue. With this point in mind, attention may be brought to the fact that, when such scattered light is predominantly blue, the magnitude of the internal-phase particles is of the order of the wave-length of light (133,134). Since the wave-length of the visible spectrum is 4,000-7,000 Å, the length of the carbon-nitrogen bond is of the order of 1.41 Å and the sum of the atomic weights of the repeating unit--methylenenitroguanidine--is 116, it is evident that chains of such a magnitude would give a molecular weight of the order of 200,000-400,000. However, Staudinger (12) has shown that colloids in solution precipitate as amorphous powders, upon the addition of a non-solvent, when the molecular weight is between 2,000 and 10,000 and as fibrous material when the molecular weight is between 10,000 and well above 100,000. It will be recalled that when ether was rapidly added to an N.G.F.P. - acetone sol, the substance was precipitated from solution as an amorphous powder which would indicate, according to Staudinger's findings, a chain-molecular weight of 2,000-10,000. Therefore, in agreement with the "micellar" theory of Mark and Meyer (11), bundles of N.G.F.P.-chain molecules are considered to be asso-

ciated laterally, by secondary valence forces, to form micelles which act as entities and which are responsible for the colloidal properties. Thus the figures 200,000-400,000 may be considered to be the order of the micellular weight, rather than the order of the molecular weight.

The formation of the N.G.F.P. plastogel may be regarded as an aggregation of N.G.F.P. micelles resulting in the formation of a fibrillar-gel structure. The formation of an xerogel or resin (by drying) may then be a continuation of this gel process, in which the micellular aggregates are brought close together and result in relatively little active surface for adsorption or solvation by liquids. The transparency of the N.G.F.P. resin can be explained by formation of an extended network in which the micelles are held together by van der Wall's forces.

The N.G.F.P. xerogel or resin was found to be more difficult to bring into solution in organic solvents than the plastogel. This may be accounted for by the presence of picric acid which was found to be retained, most probably by salt formation, but which does not enter the basic polymeric structure. The picric acid so retained may participate in holding the micelles more firmly by the establishment of associated dipoles or hydrogen bonds as the fibrillar gel structure becomes more compact in resin formation. Cold, concentrated hydrochloric acid, however, appears to be readily capable of disrupting these secondary valence forces, dispersing the N.G.F.P. micelles

and of releasing the picric acid from the polymeric structure.

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

An explosive polymer of resin type was prepared by a picric acid-catalysed polyreaction between nitroguanidine and formaldehyde, having an explosive force of 61% that of T.N.T.

An unstable intermediate, mono-methylolnitroguanidine, is formed by a freely reversible reaction requiring an excess of formaldehyde for its formation.

In the presence of added picric acid, mono-methylolnitroguanidine is transformed into a polymeric gel which cures to a thermoplastic resin.

Solutions of the polymer display the properties of a micellular, lyophilic-colloidal system.

The polymer is composed of long-chain molecules of repeating structural unit, methylenenitroguanidine.

Picric acid is retained as a resinous complex, but does not enter the basic polymeric structure.

The rates of formation of fractions containing "short", "intermediate", and "long" chains were studied relative to one another. The data indicate that upon the addition of picric acid, mono-methylolnitroguanidine almost immediately disappears with the formation of a polymerizing factor which is probably methylenenitroguanidine. From this polymerizing factor there is an apparent continuous transition through "short"- and "intermediate"- to "long"-chain molecules by a series of consecutive reactions.

The cured, pulverized resin can be press-molded into buttons or extruded into cords, and viscous solutions of the resin can be cast and cured in molds.

The cured, pulverized resin burns extremely vigorously with a brilliant flame when the oxygen content is balanced by mixing with various oxygen carriers. By choosing suitable oxygen carriers, the rate of burning can be controlled. Burning mixtures can be pelleted which contain various proportions of strontium nitrate-oxygen balanced resin, magnesium powder and calomel. They have a longer burning-time and burn with a greater intensity of red light and less luminescent-white light than the Standard Tracer Composition used in the 17 pounder A.P. shell.

High explosive plastic-masses can be made from the polymer containing up to 90% R.D.X. which can be cast-molded to give a smooth, coherent casting. These materials are less sensitive than R.D.X. and Tetryl but more sensitive than T.N.T.

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B. Crystal Size-Reduction of Nitroguanidine (Picrite[a]) by Acidic Aqueous Formaldehyde Solution

(a) Due to the industrial nature of this problem, the industrial name, picrite, will be used interchangeably with nitroguanidine.

TABLE OF CONTENTS

INTRODUCTION

Picrite is used in the preparation of flashless-cordites and its state of subdivision is known to have an important bearing on the manufacture and physical properties of the cordite. The normal process of manufacturing picrite does not lend itself to the production of crystals beyond a certain degree of fineness. In view of this limitation it was desired to develop a method for the manufacturing of ultra-fine picrites and thereby obtain a finer and more uniform product. This type of picrite is particularly desirable in flashless-cordites for larger guns in order to maintain the density of the cordites and to improve the regularity of ballistics.

Techniques have been developed whereby supersaturation of solutions can be controlled to deposit crystals of a uniform and desired size on crystallization (1). The formation of needle-shaped crystals is said to be favoured by supersaturation, especially by local supersaturation arising from local currents around growing crystals or from local cooling effects (2).

The use of protective agents for controlling the particle size during recrystallization from solution is a well known principle in industrial practice. In general the adsorption of dissolved protective agents or foreign materials (inorganic

or organic) either as ions or as polar molecules can hinder the formation of large crystals. It has long been known (3,4,5,6) that simple forms of crystals which originate from a solution can vary when the solution contains certain dissolved foreign materials.

Supersaturation may be imagined as a molecular condition in which the uniformly spaced molecules of a substance in solution, being like distances apart, exert equal attractions on each other in all directions, so that no two can come closer together than others. They all may become gradually closer as concentration increases, say by cooling, without disturbing the equilibrium of attractive forces. Anything that will destroy this will permit the molecules to cluster together. The greater the intermolecular tension, the quicker the reaction and the greater the number of clusters of molecules, that is, the greater the number of centers toward which molecular condensation will take place. The greater the number of centers of crystallization, the greater the number of crystals in a given volume and the smaller their size (7).

In crystallizations, smaller crystals are obtained (8) when the surface tension between the solid and the liquid is small, because nuclei form more easily and copiously when the surface tension is smaller. The adsorption of a dissolved foreign substance on a solid, from solution, diminishes the surface tension between the liquid and the solid and accordingly smaller crystals are deposited from solutions containing such

foreign substances.

When adsorption takes place in the crystal lattice of the tiny elementary crystals, it is called inner adsorption; when adsorption occurs upon the crystal lattice, it is called outer adsorption and such adsorption by crystals is very similar in nature to that of a colloid (9).

The use of agents for controlling picrite particle size during recrystallization from aqueous solution has been investigated intermittently over a period of 12 to 15 years and numerous agents (called protective agents) for restricting crystal growth have been examined.

Research carried out at the Armament Research Department (10) showed that ammelide, gelatin and methyl cellulose caused a certain restriction of crystal growth in picrite. Ammelide caused a reduction of the crystal width but the length was almost unaffected. On the other hand, gelatin and methyl cellulose decreased the length of the crystals but the width was little affected.

The American Cyanamid Co. claimed (11) that ethylene diamine produced a marked effect. A series of experiments was made at Woolwich using ethylene diamine in aqueous solution in various concentrations, to give a finer product than had previously been obtained. Using ethylene diamine as a protective agent, the Welland Chemical Works, Niagara Falls, Ont. were able to produce a picrite, the average dimensions of which were 2.0 x 33.2 microns. (Welland picrite by normal manufacture has

average dimensions of 3 x 70 microns).

A large number of amino- and other nitrogen compounds which have been tried at Woolwich include ammelide, gelatin, ammelide plus gelatin, cyanuric acid, dicyandiamide, urea, oxamide, amidol, nitrodicyandiamidine, m- and p-phenylene-diamine, guanidine, nitrophenyltriethanolamine, methylamine, diethanolamine, triethanolamine, phenyltriethanolamine, hexa-mine, melamine.

Only two such materials gave size-reduction of the same order as ethylene diamine, viz.: methylamine and ethylamine.

It was pointed out that these amines apparently produce simultaneous restriction of growth at all crystal faces, since there was no observed change in crystal habit.

Tanberg and Kramer (12) found that picrite could be ob-tained in finely divided form by dissolving nitroguanidine in water under superatmospheric pressure, at a temperature above 100°C.; this solution is then discharged into a cold liquid medium such as water to effect precipitation of the nitroguani-dine. By this method a product was obtained of average crystal dimensions, 3 x 20 microns.

The effect of rapid crystallization of picrite from aqueous formaldehyde solutions up to 5% concentration, by pouring the hot solution onto chopped ice, was investigated at the Armament Research Department (13).

According to a report on this investigation, the crystal size decreases progressively with increase in concentration

of formaldehyde up to 1%; but thereafter no marked change is produced. A 0.5% formaldehyde solution gives a mean crystal size of 1.5-2 x 40-50 microns.

The presence of small amounts of ammonia (0.1% solution) in conjunction with the formaldehyde is reported to have a marked effect in enhancing the degree of size-reduction. Thus a solution containing 0.5% and 0.1% of formaldehyde and ammonia respectively gives a mean crystal size of 0.5-1 x 10 microns and a specific surface of approximately 80,000 cm^2/cm^3. A 1% solution at least of methylamine is required to produce a picrite of similar size: on a weight basis, therefore, formaldehyde has more than double the efficiency of methylamine for this purpose.

It is further reported that, from solutions of 0.75% and higher of formaldehyde in the presence of ammonia, picrite crystallizes in a new form (spherulites) consisting of spherical particles about 10 microns in diameter. This type of picrite is said to be sandy to the touch and crushed with difficulty to give fine particles. These spherulites are reported to be characterized, under crossed nicol-prisms by a black cross which intersects the whole spherulite. In the presence of ammonia and amines such as methylamine the particles of size-reduced picrite are reported, in many instances, colored yellow and brown and containing yellow gelatinous lumps.

In summary it may be said that those materials which modify the crystal dimensions of picrite during its deposition from

aqueous solution are:

(a) Those which produce alteration of the crystal habit by causing restriction of crystal growth along certain parallel planes.

This may result in the formation of crystals of a "platy" nature where the restriction is at right angles to the crystal length, as is the case with ammelide or of much shortened broad needles as with gelatin or methyl cellulose.

The effect is, therefore, not one of true size-reduction; although one dimension is reduced the other two are increased or but little different from those obtained in the absence of any such agent.

(b) Those which cause no alteration in the crystal habit, but produce restriction of growth simultaneously on all crystal faces.

These are to be regarded as true size-reducing agents. Into this class fall the agents, formaldehyde, methylamine and other amines.

The features associated with these agents are: (a) They have the common property of readily reacting with picrite to give compounds. (b) They have the common property of being polar molecules as is picrite itself.

Sulphuric acid also falls into this group. It has long been known that nitroguanidine, precipitated from solution in concentrated sulphuric acid, gives a fairly fine product, and

it has been reported (14) that nitroguanidine forms a sulphate with sulphuric acid which is readily decomposed by drowning in water.

It has also been reported (15) that methylamine and other amines react with nitroguanidine to give compounds with evolution of ammonia.

In this laboratory it was found that formaldehyde and nitroguanidine undergo a reversible reaction in aqueous solution, under acidic conditions, to give mono-methylolnitroguanidine (16). The isolation of this material requires the presence of at least two moles of formaldehyde per mole of nitroguanidine. It is a very unstable compound; heating the crystalline form or its aqueous solution causes decomposition with evolution of formaldehyde and recovery of nitroguanidine.

The choice of size-reducing agents for picrite is therefore less random when restricted to the examination of compounds that readily react with it, and are of a polar nature. The effect is presumably related to the adsorption at all crystal faces of a molecular film of polar molecules or a film of ions which interfere with the deposition of layers on the crystal faces. Broukére (17) says that when ions of one charge are adsorbed, the ions of opposite charge are held by electrostatic attraction.

In the case of commonly known protective agents such as gelatin, preferential adsorption of the agent, along certain faces only, would appear to occur.

The yellow and brown coloration and the presence of yellow

gelatinous lumps, obtained at the Armament Research Department, when size-reduction of picrite was obtained by crystallization from dilute formaldehyde solutions in the presence of ammonia is considered, in this laboratory, to have resulted from products of nitroguanidine de-arrangement in hot aqueous solution. This de-arrangement is catalysed by the presence of ammonia (18).

For this reason it was decided, in this laboratory, to investigate the production of ultra fine picrite crystals by re-crystallization from dilute formaldehyde solutions in conjunction with acidic protective agents.

EXPERIMENTAL

I. Preliminary Laboratory Experiments

It was found that small quantities of sulphuric acid used in conjunction with dilute formaldehyde solutions gave a marked effect in enhancing the degree of picrite size-reduction.

In production practice the method of picrite crystallization is shock-cooling by the spray method. In the following experiments, shock-cooling was obtained by rapid pouring of the hot picrite solutions onto crushed ice with vigorous mechanical stirring.

Experimental Procedure

The standardized procedure for these investigations was as follows: 3 g. picrite were added to 50 ml. water in a 400-ml. beaker. The mixture was heated until a clear solution was obtained. The protective agent (or agents) was then introduced and the solution heated to boiling and maintained for a specified time at the boiling-point, after which the solution was shock-cooled by rapidly pouring the contents of the beaker onto a bed of crushed ice 2-2.5 in. deep contained in a 400-ml. beaker. Vigorous mechanical stirring was maintained throughout the latter operation to reduce the possibility of crystal growth. Short periods of heating were chosen, as it is obviously undesirable in production practice to prolong the spraying cycle unduly and to reduce

any de-arrangement of picrite which may occur on prolonged heating.

Microscopic estimates of crystal size and relevant remarks are contained in Tables I, II, and III.

The source of picrite used in these experiments was the finished product No. 3 as shipped from the Welland Chemical Works, Niagara Falls, Ont. It was composed entirely of needles covering a very wide range of size, 4-9 x 22-180 microns. The mean crystal size was approximately 5 x 110 microns.

When formaldehyde was used alone as the protective agent, the fine picrites gave gelatinous precipitates which did not readily separate from the mother-liquor, but were readily separated on Whatman No. 1 filter paper, in a Buchner funnel with suction supplied by a water pump.

When formaldehyde was used in conjunction with sulphuric acid, curdy precipitates were obtained which separated rapidly from the mother-liquor and were retained on a Whatman No. 1 filter paper in a Buchner funnel with suction supplied by a water pump.

The solubility of picrite is noticeably increased in formaldehyde solution and increases as the concentration of formaldehyde is increased. This fact was observed from the temperatures at which solution of the picrite occurred.

The time elapsing between pouring of the hot solution onto chopped ice and the first general appearance of a precipitate increases as the concentration of sulphuric acid is increased.

TABLE I

Variation of Picrite Crystal Size with Formaldehyde Concentration

(Concentration of Picrite Solution throughout: 3 g./50 cc.)

Run No.	Conc. of Protective Agent	Time of Heating	Mean Picrite Crystal Size	Remarks
1	1.0%	5 min.	2x18 microns	A gelatinous precipitate which precipitated immediately on shock-cooling. Composed entirely of needles of fairly uniform dimensions.
2	0.5%	5 min.	2x36 microns	A gelatinous precipitate which precipitated immediately on shock-cooling. Composed of needles not as uniform in size as those in Run No. 1.
	Heating of the 1% formaldehyde solution of picrite for a shorter period of time did not give a maximum decrease in crystal size, e.g.,			
3	1.0%	2.5 min.	2x27 microns	A gelatinous precipitate which precipitated immediately on shock-cooling. Composed of needles of fairly uniform dimensions.

1% CH_2O means 0.58 mole per 1.0 mole picrite

0.5% CH_2O means 0.32 mole per 1.0 mole picrite

TABLE II

Variation of Picrite Crystal Size from 1% Formaldehyde Solutions with Concentration of Sulphuric Acid

(Concentration of Picrite Solution throughout: 3 g./50 cc.)

Run No.	Conc. of CH_2O	Conc. of H_2SO_4	Time of Heating	Mean Picrite Crystal Size	Remarks
4	1.0%	5.0%	5 min.	0.5 x 7 microns	A very curdy precipitate appearing 50 seconds after shock-cooling. Composed of soft agglomerates which are broken up to spherulites of mean diameter 18 microns. These spherulites are hard and are broken up with difficulty to give tiny needles.
5	1.0%	1.0%	5 min.	0.5 x 7 microns	A very curdy precipitate appearing 25 seconds after shock-cooling. Composed of agglomerates not as coarse as those in Run No. 4 which are broken down to give spherulites of mean diameter 9 microns. These spherulites are broken down with difficulty to give tiny needles.
6	1.0%	0.1%	5 min.	1 x 14 microns	A gelatinous precipitate appearing 7 secs. after shock-cooling. Composed of needles covering a range of 0.5 x 5 - 3 x 45 microns

Note: (1) The spherulites on close examination appear to be of a fibrous nature consisting of radial needles. They are broken down with difficulty by a cover-glass.
(2) 1% CH_2O means 0.58 mole per 1.0 mole of picrite.
0.5% CH_2O means 0.32 mole per 1.0 mole of picrite.

TABLE III

Variation of Picrite Crystal Size from 0.5% Formaldehyde Solutions with Concentration of Sulphuric Acid

(Concentration of Picrite Solution throughout: 3 g./50 cc.)

Run No.	Conc. of CH_2O	Conc. of H_2SO_4	Time of Heating	Mean Picrite Crystal Size	Remarks
7	0.5%	5.0%	5 min.	1.0 x 7 microns	Very curdy precipitate appearing 15 seconds after shock-cooling. Composed of grains or spherulites of mean diameter 9 microns which break up fairly easily to give the needles.
8	0.5%	1.0%	5 min.	2 x 27 microns	Somewhat gelatinous precipitate appearing 4 seconds after shock-cooling. Composed of needles of not very uniform dimensions.

1% CH_2O means 0.58 mole per 1.0 mole of picrite
0.5% CH_2O means 0.32 mole per 1.0 mole of picrite

In the absence of sulphuric acid very little supersaturation occurs and precipitation is almost immediate.

It has been observed that with concentrations of formaldehyde higher than 1%, the time elapsing between shock-cooling and precipitation becomes noticeable. Further, the yield of picrite with concentrations of formaldehyde higher than 1% is decreased, presumably because of the higher solubility of picrite in the solutions. The spherulites under crossed nicol-prisms show up as white spheres intersected by a black cross.

Upon close microscopic examination these spherulites appear to be of a fibrous nature, made up of exceedingly fine radial needles radiating from an aggregate center.

From these results it appears that the picrite crystal size decreases as the formaldehyde concentration increases, and that the use of dilute sulphuric acid, in conjunction with the formaldehyde, brings about a further decrease in crystal size; increasing the sulphuric acid concentration causes the crystals to pass to a stage where small spherulites are formed.

It appears that by suitably choosing the concentrations of the protective agents, formaldehyde and sulphuric acid, a choice of crystal sizes may be obtained in needle-form or spherulitic form as desired.

The refractive index along the length of these size-reduced picrite crystals was 1.52 and the melting-point was 232-238°C. Thus, these materials are indeed picrite.

In another experiment, 3 g. picrite were dissolved in 50 ml.

water. After heating and immediately before recrystallization, formaldehyde was added to give a 1% solution. The solution was immediately shock-cooled in the described manner to give picrite crystals of about 2 x 50 microns.

This procedure would make formaldehyde available for adsorption but would not allow appreciable reaction to take place between the picrite and formaldehyde.

It was seen that when the heating time was increased from 2.5 to 5 minutes (Runs Nos. 1 and 3) a finer product was obtained upon crystallization. This phenomenon was also observed with increasing concentration of sulphuric acid used in conjunction with formaldehyde and is no doubt related to the extent of interaction of the protective agent and picrite since it is known that formaldehyde and nitroguanidine react to give mono-methylolnitroguanidine in acid medium.

The sulphuric acid may play a dual role: (a) of acting as a catalyst in the formation of mono-methylolnitroguanidine and (b) of forming a reaction product itself with nitroguanidine, i.e. nitroguanidine sulphate.

Picrite crystallized from dilute formaldehyde in the presence of sulphuric acid gives a greater reduction in crystal size for the same period of heating than does formaldehyde alone.

Two further experiments were carried out in which mono-methylolnitroguanidine was substituted for picrite and formaldehyde in the following manner:

(a) In 50 ml. water, 3.87 g. mono-methylolnitroguanidine

were dissolved. After 5 minutes of heating at the boiling-point the solution was shock-cooled in the described manner.

(b) In 50 ml. water, 3.87 g. mono-methylolnitroguanidine were dissolved. Sulphuric acid was added to give a 1% solution. After 5 minutes of heating at the boiling-point the solution was shock-cooled as previously described.

In both of these experiments picrite crystallized out after shock-cooling. Microscopic estimates of crystal size and relevant remarks are contained in Table IV.

The amount of mono-methylolnitroguanidine corresponds, upon hydrolysis, to a larger concentration of formaldehyde than 1%, and since the starting material, in these experiments, is the reaction product of formaldehyde and picrite, a much finer product might be expected upon shock-recrystallization. The presence of sulphuric acid gave a further reduction of crystal size which also might be expected since it can form a water-decomposable compound with picrite. These results indicate that the reaction product, mono-methylolnitroguanidine, plays a major role in the reduction of picrite crystal size by formaldehyde solution.

In general, the action of formaldehyde in restricting crystal growth of picrite is probably due to:

(a) The effect of shock-cooling and supersaturation of picrite solutions which causes a rapid formation of a large number of centers of crystallization.

(b) A reversible reaction between formaldehyde and picrite

TABLE IV

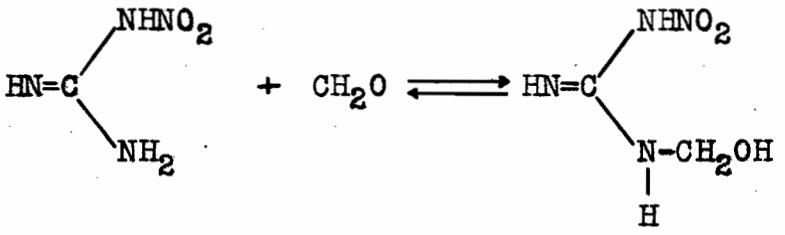
Picrite Crystal Size after Shock-Cooling Solutions of Mono-methylolnitroguanidine

(Concentration of Mono-methylolnitroguanidine solution: 3.87 g./50 cc.)

Run No.	Conc. of Sulphuric Acid	Time of Heating	Mean Picrite Crystal Size	Remarks
9	0%	5 min.	1.0 x 7-9 microns	A curdy precipitate precipitated 210 seconds after shock-cooling. Composed of a mixture of fine needles and soft agglomerates giving spherulites of mean diameter 9 microns when broken down by rubbing on a slide.
10	1.0%	5 min.	Spherulites 4.5 x 4.5 microns (a)	Composed entirely of tiny spherulites of very uniform diameter of 4.5 microns which were very difficult to break down. This run gave a very curdy precipitate after 35 seconds from shock-cooling.

(a) The spherulites formed in these two experiments showed a black cross under crossed nicol-prisms and on closer microscopic examination appeared to be composed of radial needles.

and subsequent adsorption of formaldehyde molecules by the elementary picrite crystals.



Although this dynamic equilibrium will be far to the left in these dilute solutions, the close proximity of formaldehyde and picrite molecules will probably enhance the orientation and establishment of an adsorbed protective layer of polar formaldehyde molecules which will restrict further vectorial arrangement of picrite crystals on the centers of crystallization. This effect is probably further enhanced by adsorption of the sulphuric acid catalyst.

II. Pilot Plant Experiments

Introduction

The following is an outline of the normal processing of picrite, at the Welland Chemical Works, Niagara Falls, Ont. with a brief description of the operations which are pertinent to the problem of picrite size-reduction.

The operations in the order of their occurrence are:

(i) Nitration (This is the plant name for this operation. It would be more appropriately named dehydration)

(ii) Dilution or Quenching.

(iii) Cooling.

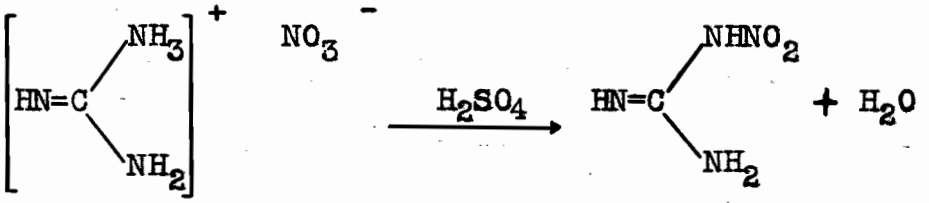
(iv) Filtration and Washing.

(v) Resolution.

(vi) Recrystallization.

(vii) Refiltration and Drying.

(i) Nitration. The function of this step is to convert guanidine nitrate (product No. 2) to nitroguanidine (product No. 3) by the removal of water with concentrated sulphuric acid at a temperature of 38-40°C.



(ii) Dilution. The function of this step is to quench the nitration solution with water or mother-liquor. Because nitroguanidine is quite insoluble in weak sulphuric acid, the bulk of the product is precipitated out at this point.

(iii) Cooling. The function of this operation is to cool the quenched nitration solution to 10°C. at which more picrite is crystallized out due to difference in solubility.

(iv) Filtration and Washing. The function of this operation is to separate the nitroguanidine crystals from the weak sulphuric acid and to wash out soluble impurities with a minimum loss of picrite.

The cooled slurry is filtered on a vacuum filter at a pressure of 22 lb. per sq. in. The resultant crude-cake contains about 60% moisture and 0.5% sulphuric acid after washing.

(v) Resolution. The function of this operation is to redissolve the crude-cake, preparatory to crystallizing it in proper crystal size.

The crude-cake, containing about 60% moisture and 0.5% sulphuric acid is mixed with water, in such proportions as to result in approximately a 7.5% solution, and heated to 100°C. by steam. After complete solution the pH is adjusted to 5.5 with soda ash to retard corrosion of the tanks, to precipitate any iron that may be in solution and to meet specifications as to pH of the finished product. The solution is not retained any longer than is necessary due to slow decomposition which is evidenced by an increase in pH and the evolution of ammonia. If the pH is allowed to rise above 7, decomposition is accelerated and ammonia may be noticed in the vapour coming off and it becomes necessary to add acid. Clarification of the solution may be required if iron hydrate is precipitated in the pH adjustment.

(vi) Recrystallization. The function of this operation is to shock-cool the solution in such a way as to form crystals averaging 3 microns in diameter by 70 microns in length, and a specific surface of 15,000 cm^2/cm^3.

The hot solution is sprayed through nozzles of 1/8 in. inside diameter. The slurry formed leaves at 35-40°C. Any final adjustments of pH are made in the slurry since tests showed that pH adjustments made here will change the pH of the crystals which is no doubt due to outer adsorption. It is necessary that the crystals be kept in constant circulation to prevent crystal growth.

(vii) Refiltration and Drying. The function of this operation is to separate the crystals from the mother-liquor and to divide the filter-cake into wafers and dry the product in a circulating air drier.

The specification for pH of the finished product ranges from 5-7.5. Normally this is met. However, during a shut-down, slight decomposition of the product may occur with a rise in pH.

It was felt at the Welland Chemical Works that the average crystal size could be reduced with smaller spray orifices and an increased spraying pressure, but this would have required new or more equipment. In view of this limitation it was considered advantageous to develop a method of manufacture of ultra-fine picrite that would not require any mechanical change in the normal production method.

It was found (19) that re-spraying of Welland picrite does not give as fine a product as that resulting from spraying Holton Heath picrite.

This difference is probably an illustration of the value of protective agents in the spraying process, since it is most easily explainable in terms of contaminants. Crystals of Welland picrite are known to have a rhombic transverse section, in general, although occasionally development of other crystal faces gives five- or six-sided crystals, but the relative lengths of the sides differ only slightly. Holton Heath picrite on the other hand possesses a six-sided figure resembling a flattened hexagon i.e. with one pair of parallel faces greatly exceeding the remainder in length.

This difference is ascribed to the presence of certain reaction by-products in Holton Heath picrite since the Welland product is of high purity; furthermore, it can be transformed into the Holton Heath type of crystal by addition of small amounts of contaminants such as ammelide.

If it is the case that the spray process can differentiate between two picrite solutions one of which contains traces of protective agent, it is evident that the introduction of small amounts of formaldehyde will have a remarkable effect.

Accordingly, it was decided to carry out all further experiments of picrite size-reduction on a semi-pilot plant scale and to simulate actual plant conditions of shock-cooling by the spray method.

Experimental Procedure

The standardized procedure for these trials was as follows. An 8000-gram solution composed of 480 g. (6%) picrite, various concentrations of protective agents and water was formed, and heated in a reaction vessel at 100°C. for a specified time.

The reaction vessel consisted of a 2-gallon, stainless-steel kettle equipped with a steam jacket, motor-driven stirring paddles and a thermometer. A thermal gauge, to determine the quality of steam supplied, was interposed between the kettle and the steam inlet.

At the conclusion of the heating period, a valve at the bottom of the kettle, was opened and the hot solution discharged into a steam-jacketed 1/2-in. pipe to which was attached a short

piece of heavy rubber tubing fitted with a spray nozzle. (The spray nozzle was made by drawing a 3-in. piece of 12-mm. glass tubing to a spray orifice of 3mm. inside diameter, which was designed to give a 9-min. spraying time of the vessel contents and a slurry temperature of 36°C. on a control run.) The hot discharging solution was sprayed by hand against the inside surface of a 20-gallon, stainless-steel, slurry tank the outside surface of which was cooled by contact with cotton aprons over which water at a temperature of approximately 10°C. was run.

During the spray procedure, the inside surface of the slurry tank was continuously scraped with a rubber paddle in order to remove any recrystallized picrite that tended to stick and lower the efficiency of shock-cooling; also the resultant slurry in the bottom of the tank was constantly agitated to prevent crystal growth.

After the total charge had been sprayed, the slurry was brought to a pH of 6-7, and the picrite separated from the mother-liquor by filtration and washed with cold water. The picrite was retained on a Whatman's No. 1 filter paper in a Buchner funnel with suction supplied by a water pump. The resultant filter-cake was broken up and dried on cloth trays in a circulating-air drier at 45°C. for 24 hours.

The effect of crystal-size and crystal form on filtration was carried out on many typical runs by measuring the volume of filtrate obtained in 15 sec. at 22 lb./sq.in., using a filter-leaf supplied by the Welland Chemical Works which was designed

to give results comparable with those in plant filtration.

The crystal form was determined under the microscope and the predominating crystal size estimated after projection on a screen at 1,000 magnification. Specific surface measurement was made by the Draft Method (20).

Spraying Experiments with Formaldehyde Solutions of Welland Finished Product No. 3 Acidified with Sulphuric, Nitric, p-Toluene Sulphonic and Benzene Sulphonic Acids.

Each 8,000-gram charge in this series of runs was made up as follows: 480 g. Welland finished product No. 3 were dissolved in 6.5 litres water which had previously been heated to 90-95°C. in the kettle. A known quantity of acid, dissolved in the remainder of the water, was run in and the solution brought to a temperature of 100°C., after which a known quantity of formaldehyde (as 40% formalin) was introduced.

Each solution was heated for a known period of time after the addition of formaldehyde, and sprayed.

The filter-cakes of Runs Nos. 2, 3, 4 and 8 were washed and reslurried with cold water to a pH of 6-7. The pH of the cold slurries of Runs Nos. 5 and 6 was adjusted from less than 2 to 6-7 with ammonia, and those of Runs No. 7 and 9 with potassium hydroxide, before filtration. All pH values were determined with universal indicator.

Run No. 1 was used as a control; no protective agents were used and no treatment of the slurry was made.

From the results assembled in Table V it is evident that extremely fine pierite can be obtained by spraying, using a suitable concentration of acid and formaldehyde.

TABLE V

Spraying Experiments with Formaldehyde Solutions of Welland Finished Product No. 3 Acidified with Sulphuric, Nitric, p-Toluene Sulphonic and Benzene Sulphonic Acid

(Concentration of picrite solution throughout: 480g./8000g. solution)

Run No.	Conc. of Protective Agents in % CH_2O	H_2SO_4	Heating Time in min.	Crystal: Form	Crystal: Size (predominating) in microns	Crystal: Specific Surface Cm^2/cm^3	Remarks
1	0 (control)	0	5	needles	4 x 100 range: 70-500	15,600	Lumpy slurry. Filtration very fast; 1000 ml./15 sec., 22 lb./sq.in.; dry cake and no cracking.
2	0.5	0.5	7	needles	1-2 x 16	36,600	Gelatinous slurry; needles appeared to be laminated with splayed ends. Filtration: 760 ml./15 sec., 22 lb./sq.in.; fairly dry cake and little cracking.
3	1.	1.	5	incipient spherulites(a)	12-15 diam.	59,000	Slightly curdy slurry; incipient spherulites of loose structure, broken down easily by rubbing on slide to give needles 3-5.4 long. Filtration: 570 ml./15sec., 22 lb./sq.in.; slow drying and some cracking of cake.
4	1.	1.	5	ditto	12-15 "	63,000	ditto

(continued on page 26)

TABLE V (continued)

Spraying Experiments with Formaldehyde Solutions of Welland Finished Product No. 3 Acidified with Sulphuric, Nitric, p-Toluene Sulphonic and Benzene Sulphonic Acid

(Concentration of picrite solution throughout: 480g./8000g. solution)

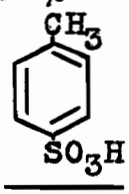
Run No.	Conc. of Protective Agents in % CH_2O	HNO_3	Heating Time in min.	Crystal Form	Crystal Size (predominating) in microns	Specific Surface cm^2/cm^3	Remarks
5	1.	0.5	5	needles and incipient spherulites	1 (or less) x 5-6 7 diam.	62,300	Slightly curdy slurry; most incipient spherulites which were broken down fairly easily by rubbing on slide to give needles 5-6 γ long. Filtration: 600 ml./15 sec., 22 lb./sq.in.; fair drying and slow cake cracking.
6	1.	0.75	6	needles and incipient spherulites	1 (or less) x 4-5 7 diam.	60,200	Very similar to above run except that incipient spherulites appeared to be a little more numerous, better developed and more difficult to break down.
7	1.	1.25	5	incipient & true spherulites	12 diam.	36,300	Very curdy slurry; mostly true spherulites. Filtration: 850 ml./15 sec., 22 lb./sq.in. Slow drying but little cake cracking

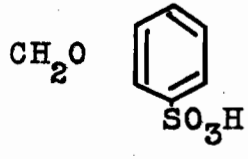
(continued on page 27)

TABLE V (concluded)

Spraying Experiments with Formaldehyde Solutions of Welland Finished Product No. 3 Acidified with Sulphuric, Nitric, p-Toluene Sulphonic and Benzene Sulphonic Acid

(Concentration of picrite solution throughout: 480g./8000g. solution)

Run No.	Conc. of Protective Agents in % CH_2O		Heating Time in min.	Crystal: Form	Crystal: Size (predominating) in microns	Crystal: Specific Surface cm^2/cm^3	Remarks
8	1	1	5	needles & incipient spherulites	1 or less x 11	65,100	Slightly curdy slurry; mostly needles; incipient spherulites of loose texture and easily broken down by rubbing on slide; Filtration: 580 ml./15 sec. 22lb./sq.in.
9	1	1	5	ditto	1-2 x 18	56,000	Very similar to above run except incipient spherulites appeared to be more numerous and better developed. Filtration: 640 ml/ 15 sec., 22 lb./sq. in.



(a) Incipient spherulites appear to be a stage intermediate between needle and true spherulite formation where the needles radiate symmetrically from the center of the aggregate.

Weight for weight, these acids appear to be of the same order of effectiveness in reducing picrite crystal size when used in conjunction with a 1% formaldehyde solution, picrite crystals of incipient spherulitic structure being formed. With increase in acid concentration it would appear that true spherulitic formation sets in with a corresponding drop in specific surface.

Supersaturation was quite noticeable with the higher concentrations of protective agents, as determined by the time elapsing between contact of the hot solution with the cold surface of the slurry tank and the first general appearance of precipitation.

Tests carried out by the Welland Chemical Works indicated that nitric acid was the least corrosive of these acids but that in general, acids of these concentrations would probably be too corrosive for use in their stainless-steel equipment. Further, the pH values of the crystals in these runs were found to be too acidic to meet specification, which was no doubt due to inner adsorption of acid since the outer crystal pH was adjusted to 6-7 in the slurry tank.

Laboratory experiments, in which hot 6% aqueous picrite solutions containing small amounts of ammonium sulphate and formaldehyde were shock-cooled by pouring onto cracked ice, showed that a considerable size-reduction had been occasioned.

Solutions containing 0.5% ammonium sulphate and 1% formaldehyde gave needles of average dimensions 1 x 12-14 microns.

Solutions containing 1% ammonium sulphate and 1% formaldehyde gave true spherulites 5-7 microns in diameter.

Similar results were obtained with ammonium nitrate and formaldehyde. No further effect was obtained by a heating period longer than 10 minutes.

It was reasoned from these results that ammonia neutralization of the sulphuric acid in a solution of Welland crude filter-cake would effect a size-reduction if used in conjunction with formaldehyde.

By this procedure pilot-plant runs were carried out.

Spraying Experiments with 1% Formaldehyde Solutions of Welland Crude-Cake with Ammonia Neutralization of Cake Acidity, and Related Experiments.

Each 8,000-gram charge in this series of runs was made up as follows: 1,215 g. Welland crude-cake, containing 60% moisture and approximately 0.5% sulphuric acid, were dissolved in 6 litres water which had previously been heated to 90-95°C. in the kettle. The pH was adjusted from less than 2 to 6-7 with ammonia and the remainder of the water run in, after which the solution was brought to a temperature of 100°C. and formaldehyde introduced (as 40% formalin) to give a 1% solution.

Upon the addition of formaldehyde the pH dropped to 5 and remained at this value throughout the heating period.

Each solution was heated for 10 minutes after the addition of formaldehyde, and sprayed.

The filter-cakes were each washed with 2 litres of cold water.

All pH values were determined with universal indicator.

The results are assembled in Table VI, and it is evident from these figures that exceedingly fine picrite is occasioned by 1% formaldehyde solution and spraying, using Welland crude-cake the acid content of which is neutralized by ammonia.

It is probable that both ammonium and sulphate ions as well as formaldehyde molecules are adsorbed by the picrite crystal faces in producing this remarkable size-reduction with corresponding high specific surface.

The concentration of ammonium sulphate does not appear to be quite sufficient to cause general true spherulitic formation. The variation of Runs Nos. 14 and 15 was ascribed to a small difference in cake acidity since a different batch of Welland crude-cake was used in these two runs.

In an attempt to produce true spherulites by the above procedure 16 g. (0.2%) ammonium sulphate and 16 g. less water was added after ammonia neutralization of the crude-cake acidity. Again the pH dropped to 5 upon the addition of formaldehyde and remained at this value throughout the heating period. The results are assembled in Table VII.

From these figures it is evident that ammonium sulphate does indeed have a profound effect on picrite size-reduction by formaldehyde solution. It appears that with increasing ammonium sulphate concentration, in a 1% formaldehyde solution, incipient spherulitic structure becomes more developed and true spherulitic formation sets in with a corresponding drop in specific surface.

TABLE VI

Spraying Experiments with 1% Formaldehyde Solutions
of Welland Crude-Cake and Ammonia Neutralization of Cake Acidity

(Concentration of picrite solution throughout: 480 g./8000 g. solution.)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal			Remarks
			Form	Size (predominating) in microns	Specific Surface cm^2/cm^3	
10	1%	10	needles & incipient spherulites	1 (or less) x 6 12-15 diam.	79,000	Gelatinous slurry, mostly needles; some incipient spherulites of loose texture and needle clusters which are broken down easily by rubbing on slide. Filtration: 450 ml./15 sec., 22 lb./sq.in.
11	1%	10	do	1 (or less) x 5-10	77,200	ditto
12	1%	10	do	1 (or less) x 5-10	77,200	ditto
13	1%	10	do	1 (or less) x 3-8	81,000	ditto

(continued on page 32)

TABLE VI (continued)

Spraying Experiments with 1% Formaldehyde Solutions
of Welland Crude-Cake and Ammonia Neutralization of Cake Acidity

(Concentration of picrite solution throughout: 480 g./8000 g. solution.)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal: Form	Crystal: Size (predominating) in microns	Crystal: Specific Surface cm^2/cm^3	Remarks
14	1%	10	needles & incipient spherulites	1 (or less) x 3-5	86,400	Similar to Runs Nos. 10 to 13 but more incipient spherulites.
15	1%	10	needles, incipient spherulites plus some fine material	1 (or less) x 3-4 3-8 diam. 1 (or less) diam.	88,200	Slightly curdy slurry; soft agglomerates of mixture; very few true spherulites. Filtration: 580 ml./15 secs., 22 lb./sq.in.

TABLE VII

Spraying Experiments with 1% Formaldehyde Solutions of Welland Crude-Cake and Ammonia Neutralization of Cake Acidity plus 0.2% Ammonium Sulphate

(Concentration of picrite solution throughout: 480 g./8000-g. solution)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal			Remarks
			Form	Size (predominating) in microns	Specific Surface cm^2/cm^3	
16	1%	10	True spherulites & fine particles	5-7 diam. ca. 1 diam.	61,900	Very curdy and thin slurry. Filters fast until some cake cracking. Mostly true spherulites; a small amount of fine particles.
17	1%	10	do	do	56,400	ditto
18	1%	10	do	do	59,700	ditto

Specimens of inhibited spherulitic formation were captured on a glass slide in the following manner.

A microscope slide, which had previously been cooled to 0°C., was rapidly coated on one side with a film of the above hot solution. By this procedure the picrite almost instantly crystallized out in essentially two dimensions to give a restricted spherulitic growth.

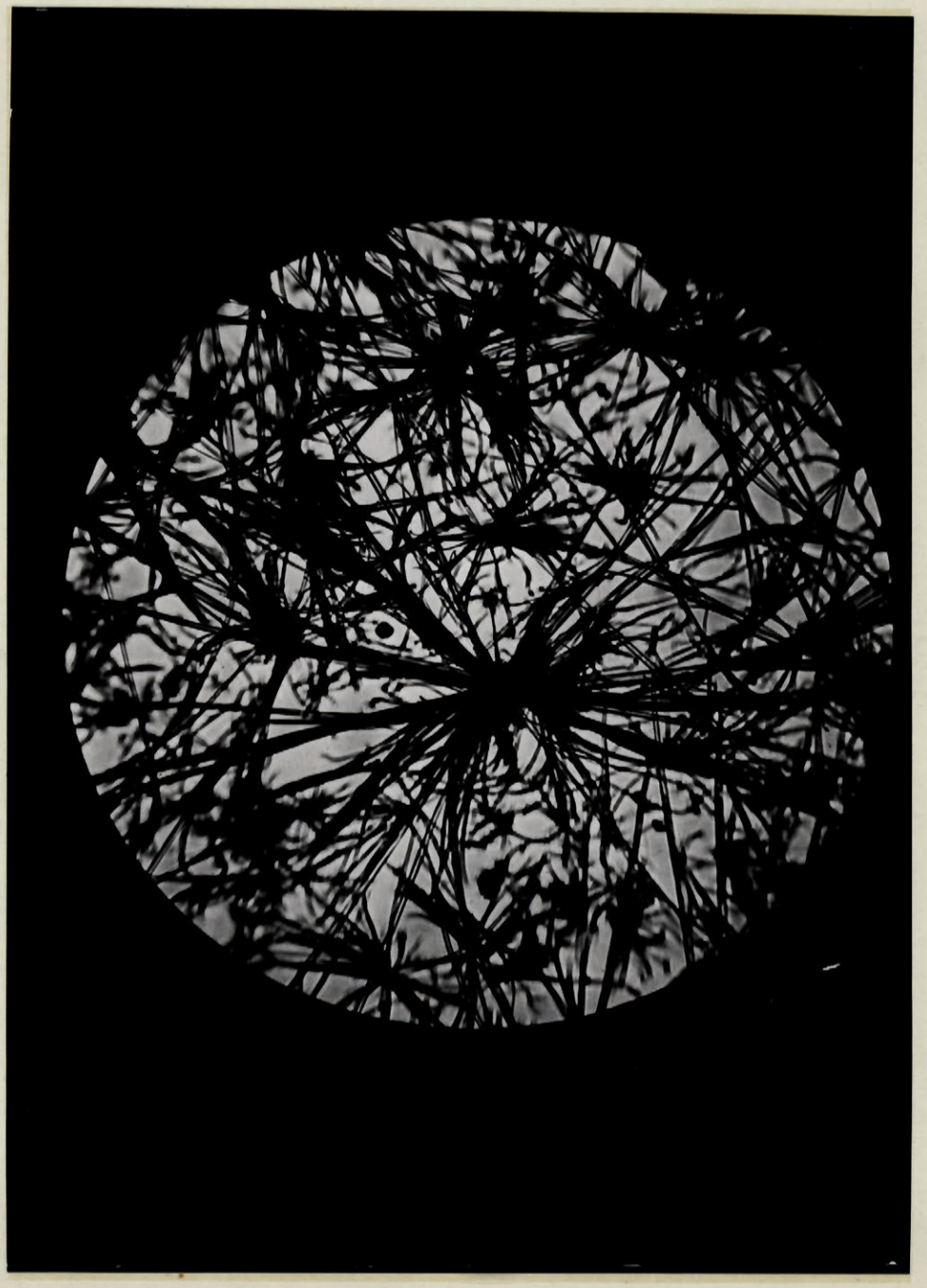
The photomicrographs (Figs. 1 and 2) indicate that spherulitic formation consists of the growth of radial needles from an aggregate center. Both specimens shown were formed on the same slide and probably show different stages in spherulitic development.

The use of ammonia for sulphuric acid neutralization or as its sulphate does not seem to cause decomposition of nitroguanidine; no yellow coloration or yellow gelatinous lumps were in evidence. Such is not the case when ammonia is used in the absence of sulphuric acid as shown by the following run.

An 8000-gram charge was made up using 480 g. Welland finished product No. 3, which is acid-free. After aqueous solution was effected and brought to a temperature of 100°C. in the usual manner, ammonia and formaldehyde were run in to give a 0.1% and a 1.4% concentration respectively.

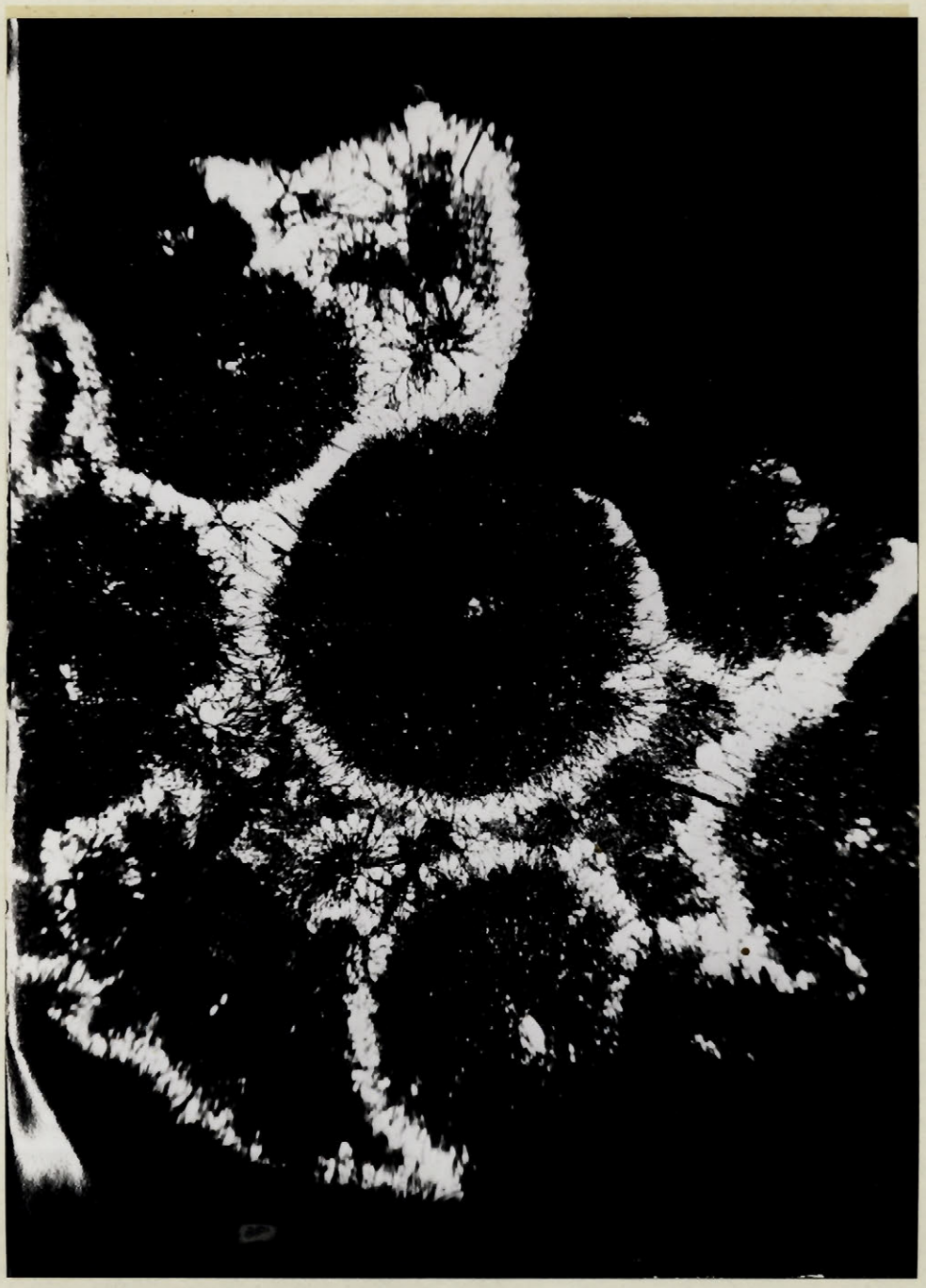
The solution was heated for 5 min. at 100°C. after the ammonia and formaldehyde addition, and sprayed.

The filter-cake was washed and reslurried with cold water to a pH of 6-7 determined by universal indicator.



Inhibited Spherulitic Formation

FIGURE 1



Inhibited Spherulitic Formation

FIGURE 2

From the results assembled in Table VIII it appears that nitroguanidine de-arrangement occurs when ammonia is used alone in conjunction with formaldehyde as a protective agent, as evidenced by yellow coloration and yellow gelatinous lumps in the product.

The effect of hexamine, which contains potential formaldehyde and ammonia, as a picrite size-reductant was determined by the following three runs.

In Run No. 20, 480 g. (6%) Welland finished product No. 3 was used in making up the 8,000-gram charge. After its aqueous solution was effected and brought to a temperature of 100°C. in the usual manner, 111 g. (1.38%) hexamine was added and the solution heated for 10 min. at 100°C., and sprayed.

In Run No. 21, 1,215 g. Welland crude-cake containing 60% moisture and 0.5% sulphuric acid, was used to make up the 8,000-gram charge containing 6% picrite. After its aqueous solution was effected and brought to 100°C., 111 g. (1.38%) hexamine was introduced and the solution heated for 10 min. at 100°C., and sprayed.

In Run No. 22, 1,215 g. Welland crude-cake was similarly used as in Run No. 21; but before addition of 111 g. (1.38%) hexamine at 100°C., the crude-cake acid was neutralized with ammonia. The total 8,000-gram charge was then heated for 10 min. at 100°C., and sprayed.

The pH of each solution after the heating period was approximately 7 as determined with universal indicator.

TABLE VIII

Spraying of a Solution of Welland Finished Product No. 3 Containing 1.4% Formaldehyde and 0.1% Ammonia

(Concentration of picrite solution: 480 g./8000-g. solution)

Run No.	Conc. of Protective Agents in CH_2O	Conc. of Protective Agents % NH_3	Heating Time in min.	Crystal: Form	Crystal: Size (predominating) in microns	Crystal: Specific Surface cm^2/cm^3	Remarks
19	1.4	0.1	5	needles, incipient and true spherulites	1 (or less) x 3-5 5-10 diam.	29,000	Curdy slurry. Filtered fast; slow drying. Yellow coloration and some yellow gelatinous lumps.

Upon complete hydrolysis 1.38% hexamine would give approximately 1% formaldehyde and 0.04% ammonia in solution. However, from the results listed in Table IX it is apparent that in the absence of sulphuric acid (Run No. 20) or in the presence of ammonia-neutralized sulphuric acid (Run No. 21), under these experimental conditions, very little hexamine hydrolysis occurs. On the other hand, in the presence of free sulphuric acid (Run No. 22), hydrolysis takes place and a considerable size-reduction of picrite is effected.

Under the same conditions of Run No. 21 a glucose concentration of 1% brought about no observable size-reduction; a specific surface of 17,000 was obtained.

Tests carried out at the Welland Chemical Works showed that traces of melamine are usually present in their picrite and, that when pH adjustments are made with ammonia, the ammonium sulphate formed breaks down on drying in the presence of melamine to form melamine sulphate and free ammonia. This phenomenon is obviously undesirable on the basis of crystal pH specifications and indeed determinations on the products of Runs Nos. 10 to 22 showed that the crystal pH values were generally between 7 and 8.

Soda-ash pH adjustments are successfully used in the production of Welland picrite to meet pH specifications of the crystal. Accordingly it was decided to effect size-reduction by heating the sulphuric acid containing crude-cake in dilute formaldehyde solution and after 10 minutes of reaction to neutralize the acid with soda-ash instead of ammonia, immediately before spraying.

TABLE IX

Spraying Experiments with Welland Picrite Solutions Containing 1.38% of Hexamine

(Concentration of picrite solutions throughout: 480 g./8000-g. solution)

Run No.	Conc. of Hexamine in %	Heating Time in min.	Crystal			Remarks
			Form	Size (predominating) in microns	Specific Surface cm^2/cm^3	
20	1.38	10	needles	2 x 40.7 range: - x 5-500	17,700	Lumpy slurry. Filtration very fast; dry cake; no cracking. Very similar to control Run No. 1. Welland finished product.
21	1.38	10	needles	1 x 11.5	56,600	Gelatinous slurry. Very uniform crystal size. Odour of CH_2O during spray. Filtered slowly with some cracking; slow drying. Welland crude-cake.
22	1.38	10	needles	2 x 34	27,900	Lumpy slurry. Filtration fast: 980 ml./15 sec., 22 lb./sq.in.; dry cake and no cracking. Welland crude-cake plus ammonia neutralization.

The following series of runs was made by this procedure using different concentrations of formaldehyde as a control of crystal size, and an efficient crystal size-reduction successfully obtained.

Spraying Experiments with Dilute Formaldehyde Solutions of Welland Crude-Cake and Soda-Ash Neutralization of Cake Acidity after Reaction.

Each 8000-gram charge in this series of runs was made up as follows: 1215 g. Welland crude-cake, containing 60% moisture and approximately 0.5% sulphuric acid, were dissolved in 6 litres water which had previously been heated to 90-95°C. in the kettle. A known amount of formaldehyde (as 40% formalin) was run in after the remainder of the water had been added and the solution brought to a temperature of 100°C.

Each solution was heated for 10 min. after the addition of formaldehyde. At the conclusion of the heating period the pH of the solution was adjusted from less than 2 to 6, and sprayed. The pH of the slurries was approximately 6 in each case.

The filter-cakes were each washed with 2 litres of cold water.

All pH values were determined with universal indicator.

From the results assembled in Table X it is evident that ultra-fine picrites are obtained by this procedure. The crystal size progressively decreases as the formaldehyde concentration increases, with a corresponding increase in specific surface which continues during the formation of loose incipient

TABLE X

Spraying Experiments with Dilute Formaldehyde Solutions of Welland Crude-Cake and Soda-Ash Neutralization of Cake Acidity after Reaction

(Concentration of picrite solution throughout: 480 g./8000-g. solution)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal			Remarks
			Form	Size (predominating) in microns	Specific Surface cm^2/cm^3	
23	0.3	10	needles	2 x 25	28,000	Lumpy slurry. Filtered fast: 900 ml./15 sec., 22 lb./sq.in.; good drying and no cracking of cake.
24	0.3	10	needles	2 x 21	28,000	ditto
25	0.5	10	needles	1-2 x 18	32,900	Somewhat gelatinous slurry. Filtered fairly fast; no cracking and fast drying of cake.
26	0.5	10	needles	1-2 x 17	...	ditto
27	0.5	10	needles	1-2 x 18	34,900	ditto
28	0.7	10	needles	1-2 x 16	40,600	Gelatinous slurry. Filtered fairly fast but showed some cake cracking.
29	0.7	10	needles	1-2 x 15	45,100	ditto

(Continued on page 43.)

TABLE X (continued)

Spraying Experiments with Dilute Formaldehyde Solutions of Welland Crude-Cake and Soda-Ash Neutralization of Cake Acidity after Reaction

(Concentration of picrite solution throughout: 480 g./8000-g. solution)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal			Remarks
			Form	Size (predominating) in microns	Specific Surface cm^2/cm^3	
30	0.7	10	needles	1-2 x 15	45,100	Gelatinous slurry. Filtered fairly fast but showed some cake cracking.
31	0.9	10	needles	1 (or less) x 10	50,500	Gelatinous slurry but thinner than previous runs. Filtered more slowly than previous runs.
32	0.9	10	needles	1 (or less) x 12	...	ditto
33	1.0	10	needles	...	55,300	Very similar to Runs 31 and 32 but filtered less quickly.
34	1.1	10	needles & incipient spherulites	1 (or less) x 5-10	65,400	Gelatinous slurry; only a few incipient spherulites of very loose texture. Filtered fairly slowly with cake cracking.

(Continued on page 44.)

TABLE X (Continued)

Spraying Experiments with Dilute Formaldehyde Solutions of Welland Crude-Cake and Soda-Ash Neutralization of Cake Acidity after Reaction

(Concentration of picrite solution throughout: 480 g./8000-g. solution)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal: Form	Crystal: Size (predominating) in microns	Crystal: Specific Surface cm^2/cm^3	Remarks
35	1.1	10	needles & incipient Spherulites	1 (or less) x 5-10	57,800	Gelatinous slurry; only a few incipient spherulites of very loose texture. Filtered fairly slowly with cake cracking.
36	1.2	10	needles & incipient spherulites	1 (or less) x 3-10 5-10 diam.	66,000	Similar to Runs Nos. 34 and 35 but more incipient spherulites and more cake cracking.
37	1.3	10	do	1 (or less) x 4-8	69,300	Gelatinous slurry; mostly incipient spherulites of loose texture which readily broke up to needles by rubbing on slide.

(Continued on page 45.)

TABLE X (Concluded)

Spraying Experiments with Dilute Formaldehyde Solutions of Welland Crude-Cake and Soda-Ash Neutralization of Cake Acidity after Reaction

(Concentration of picrite solution throughout: 480 g./8000-g. solution)

Run No.	Conc. of CH_2O	Heating Time in min.	Crystal			Remarks
			Form	Size (predominating) in microns	Specific Surface cm^2/cm^3	
38	1.3	10	needles & incipient spherulites	1 (or less) x 4-8	70,700	Gelatinous slurry; mostly incipient spherulites of loose texture which readily broke up to needles by rubbing on slide.
39	1.5	10	do	1 (or less) x 4-8	65,200	Slightly curdy slurry. Filtered slowly: 500 ml./15 sec., 22 lb./sq.in. with cake cracking. Incipient spherulites appeared to be slightly more developed than in previous runs, and harder to break down on slide.
40	1.5	10	do	1 (or less) x 4-8	64,000	ditto
41	1.5	10	do	1 (or less) x 4-8	65,600	ditto

spherulites. When the incipient spherulites become a little more developed there is a slight decrease in specific surface.

Further Considerations of Size-Reduced Picrite by Pilot-Plant Spraying

The specific surface of Welland finished product No. 3 ranges from 10,000 cm^2/cm^3 to 18,000 cm^2/cm^3 and averages approximately 15,000 cm^2/cm^3 in plant production by the normal process. The specific surface of the picrite obtained in the control run (Run No. 1) was seen to be 15,600 cm^2/cm^3. Thus it is apparent that the spraying method, developed in the pilot plant, compares favourably in efficiency with actual plant spraying.

The photomicrographs (Figs. 3 to 7 of 200 magnification) illustrate how the control sample, in the absence of any protective agent compares with samples of picrite recrystallized by pilot-plant spraying picrite solutions which have been heated with small quantities of formaldehyde under acidic conditions.

In general terms it may be said that, as the concentration of protective agents increases, the crystal size decreases and then passes through a stage of incipient spherulites where the needles radiate symmetrically from the center of the aggregate. Beyond this, true spherulitic formation sets in. Also, as the crystal size decreases, the specific surface increases. This increase in specific surface continues in the formation of loose incipient spherulites until they become more developed and then decreases as true spherulitic formation sets in.

During the course of these experiments, various degrees of incipient spherulitic formation were obtained. The forma-

tion appears to progress with increase in protective agent concentration, from loose clusters of needles to fairly compact radial aggregates beyond which true spherulites are obtained. The black cross which intersects these spherulites, under a polarizing microscope, becomes more clearly seen until in the case of true spherulites it is very distinct. (See Fig. 7)

Spherulitic formation appears to be a known phenomenon of rapid crystallization in the presence of foreign material. It is known to occur in geological formations, where rapid cooling of magmas has taken place and it is therefore often found in rock glasses. The spherulites thus formed appear to consist of prismoid or tabular crystals radiating from a point (21). The photomicrographs (Figs. 1 and 2) of inhibited spherulitic formation, obtained by a method previously described, indicate that a similar radial structure exists in picrite spherulites.

Under a polarizing microscope, a needle of picrite becomes extinct along its length every 90°, as the stage is rotated. Thus in a compact spherulitic structure, consisting of needles radiating from an aggregate center, those needles which lie in the positions of extinction will appear dark, and quarter the spherulite by a black cross. As the stage is rotated, other needles move into the positions of extinction and the cross should remain stationary. This is indeed the case.

Therefore, since it is evident that picrite spherulites are composed of tiny needles, their formation is not regarded

as essentially an alteration of crystal habit. As in the formation of ultra-fine needles of picrite, the protective agents are considered to be adsorbed by all the faces of the elementary crystals during shock-recrystallization to effect true size-reduction.

These picrite particles in the form of fine spheres are interesting in that they may prove of importance for the manufacture of certain types of propellent. Batches prepared in the pilot plant are now being investigated for their behavior in cordites by C.A.R.D.E., Val Cartier, Que.

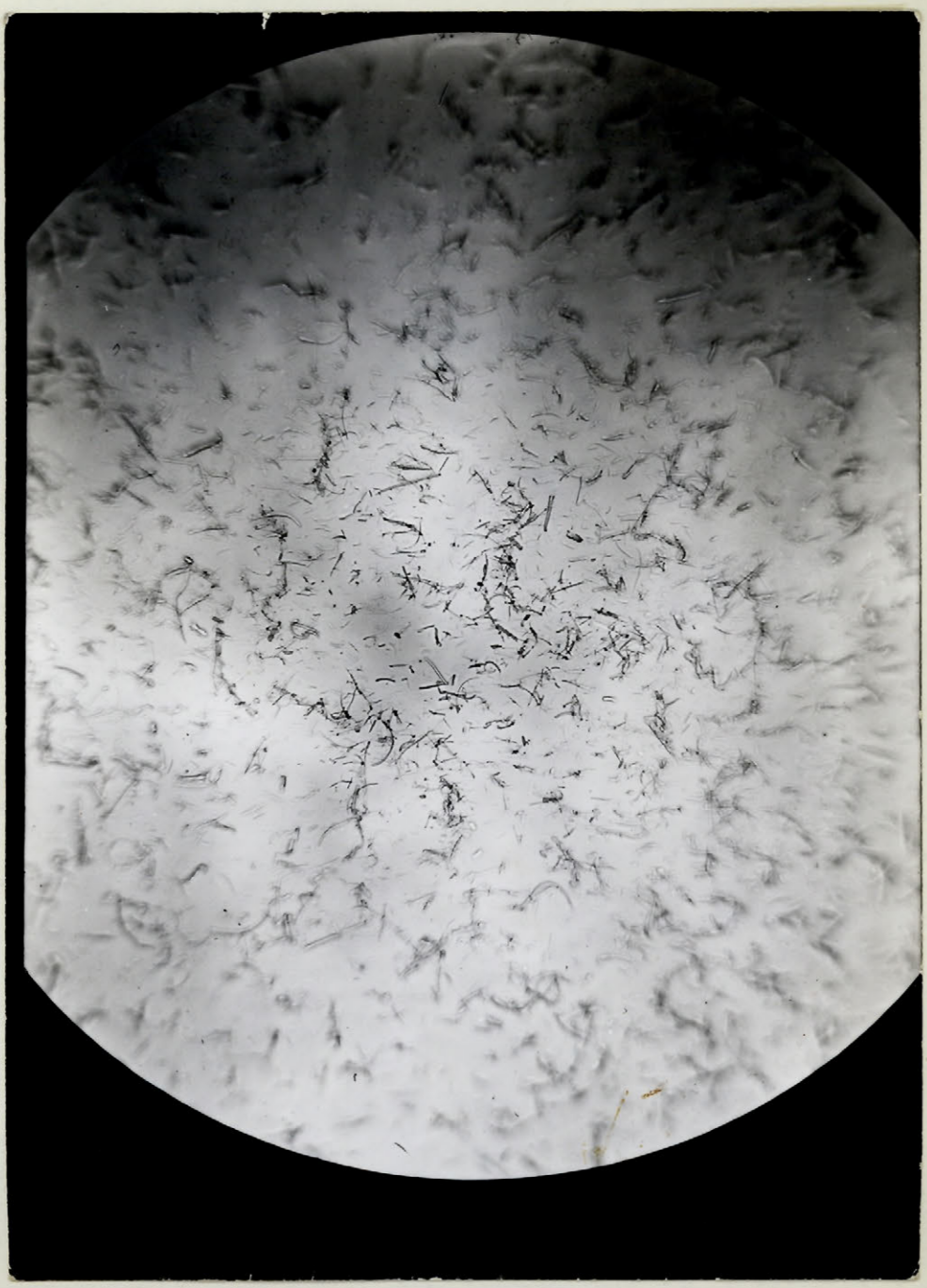
A study of the photomicrograph (Fig. 3) of the relatively large needles obtained in the control run will show that tiny bubbles have been occluded in the picrite crystals. Such occlusions are likely to trap impurities when recrystallization occurs in solutions containing protective agents. It is known that a certain amount of crystal breakage takes place during the incorporation of picrite into cordites. Therefore, because of these occluded bubbles and because of inner adsorption which probably occurs, it is evident that pH adjustment should be made in picrite solutions before recrystallization in order to meet crystal pH specifications.

Soda-ash has been found to be a successful agent for this purpose in acidic picrite solutions and this is the procedure used when crystal size-reduction has been brought about by recrystallization of picrite from acidic dilute solutions of formaldehyde (Runs Nos. 23 to 41).

Thus, a method for the production of ultra-fine picrites was developed, which is superior to previous methods. By this procedure, no decomposition seems to occur, pH control for crystal specifications is possible and no alteration of the sequence of plant production is required. Addition of formaldehyde and the heating period followed by soda-ash neutralization is permitted in the normal resolution stage just previous to spraying.

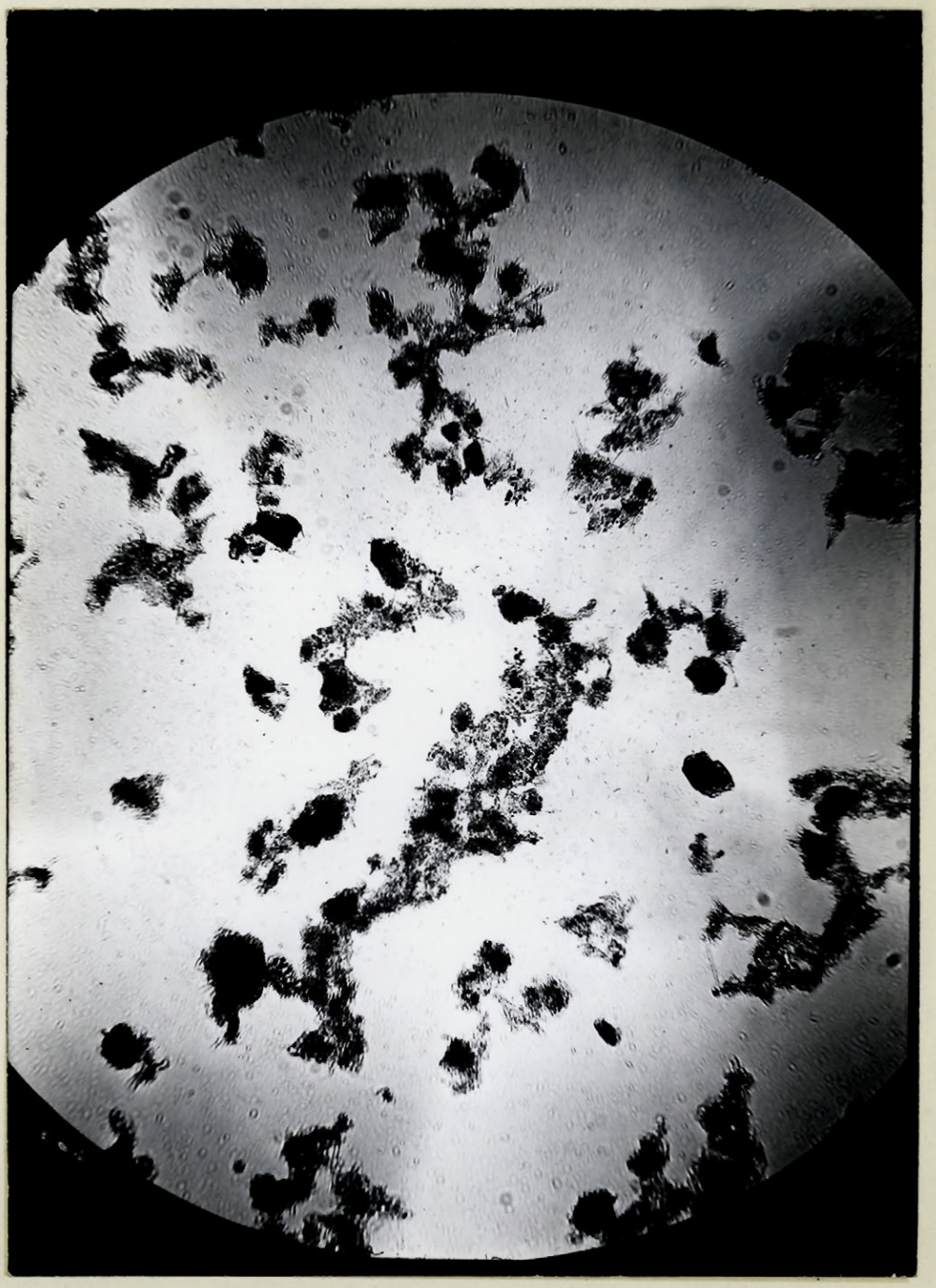
Specific Surface - 15,600 cm^2/cm^3

FIGURE 3 (Control)



Specific Surface - 65,600 cm^2/cm^3

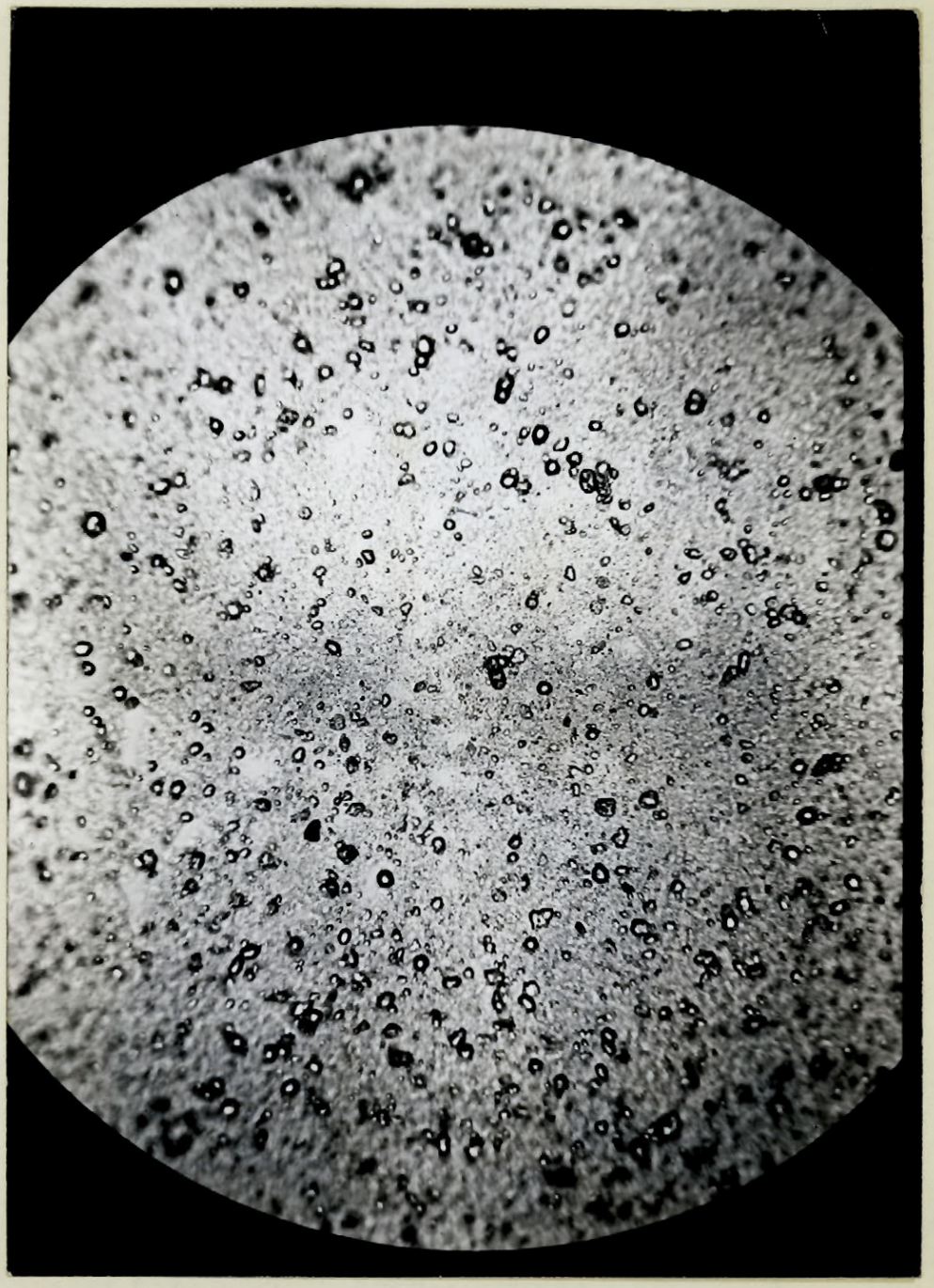
FIGURE 4



Loose Incipient Spherulites

Specific Surface - 60,200 cm^2/cm^3

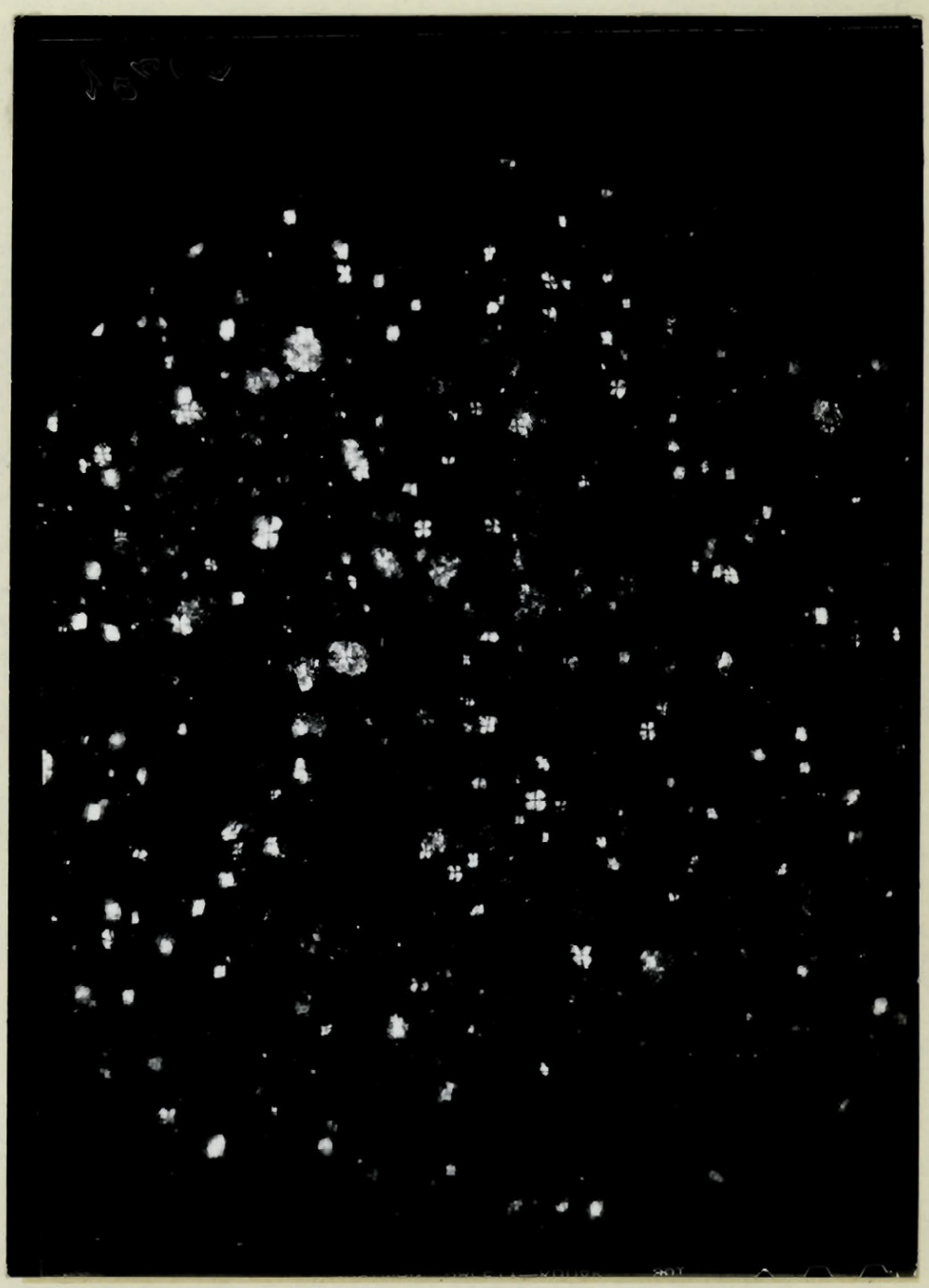
FIGURE 5



True Spherulites

Specific Surface - 30,300 cm^2/cm^3

FIGURE 6



True Spherulites Showing Black Cross Intersecting the Whole Spherulite Under Crossed Nicol-Prisms

FIGURE 7

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

Ultra-fine nitroguanidine crystals were prepared by shock-recrystallization, after heating in dilute acidic formaldehyde solutions.

Shock-recrystallization was obtained by a semi-pilot plant adaptation of the known spray method used in the normal manufacture of nitroguanidine.

The acidic components used in conjunction with formaldehyde include: nitric, p-toluene sulphonic, benzene sulphonic, and sulphuric acids, and ammonium sulphate.

Formaldehyde in the presence of acidic agents causes a greater restriction of crystal growth than formaldehyde alone.

From laboratory experiments, the restriction of crystal growth appears to be due to (a) the rapid formation of a large number of centers of crystallization and (b) the adsorption of a film of protective agents which is related to a reversible reaction between nitroguanidine and formaldehyde.

As the concentration of formaldehyde and acidic agent increases, the crystal size decreases with a corresponding increase in specific surface. Beyond this the crystals pass through a stage of increasing spherulitic development from incipient to true spherulites.

Experiments showed that the nitroguanidine spherulites are composed of compact needles radiating from an aggregate center.

On the basis of crystal pH specification and application to plant production the most satisfactory method is by heating dilute formaldehyde solutions of crude, acid-containing nitroguanidine and adjusting the pH with soda-ash immediately before spraying.

By this process the crystal size and specific surface are controlled by varying the formaldehyde concentration. Thus, from solutions containing 0.3% to 1.3% formaldehyde there is a continuous decrease in crystal size and increase in specific surface from 2 x 25 microns and 28,000 cm^2/cm^3 to less than 1 x 4-8 microns and 70,700 cm^2/cm^3 respectively.

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