THE GELATION OF NITROCELLULOSE

by

Fredrich Herbert Olsen

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Bachelor of Science

from the
Massachusetts Institute of Technology

1942

Signature of Author _______________________
Certification of Supervisor ___________________
Head of Department ________________________
Prof. George W. Swett,
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Sir:

Herewith I take pleasure in presenting
the Scientific Bachelor's Thesis, "The Gelation of Nitrocellulose", submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in the Department of Chemical Engineering.

With the hope that this work will prove useful to those interested, this thesis is,

Respectfully submitted,

Fredrich Herbert Olsen
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I. SUMMARY

The Ball Powder Process for the manufacture of military smokeless powder developed by the Western Cartridge Company of East Alton, Illinois, presents a new problem in the technique of powder making, that of the complete dispersion of nitrocellulose. It is the purpose of this thesis to study that dispersion and to find a means of differentiating between nitrocelluloses some of which give unsatisfactory graining characteristics.

Microscopic observation with photographs of the dispersion process with varying concentrations of the solvent, ethyl acetate, was the principal method used.

It was found that the dispersion of nitrocellulose was very complex, involving three stages: a short period in which the fresh solvent leached from the surface of the fibre the more dispersable nitrocellulose; then an intermediate period of fairly uniform swelling which occurred parallel to the axis of the fibre; followed by a rupture of the cell wall structure and a radial disintegration of the fibre mass into the solvent.
It was suggested that the principal mechanism of the dispersion was the hydrolysis of the ethyl acetate with the formation of loose addition compounds and that the time of dispersion could possibly be shortened by finding a suitable catalyst for that hydrolysis. Furthermore, the time for complete dispersion under ideal conditions was considerably shorter than the time allowed of one hour; and was probably more in the order of a couple of minutes.

Various samples of nitrocellulose having different nitrogen contents showed marked differences in the minimum concentration of ethyl acetate in which they would disperse. The nitrogen content and the dispersability showed a direct linear correlation, in that the higher the nitrogen content, the more dispersion resistant the pulp became. It was suggested that the explanation of this phenomenon could be the decrease in polar moment with the greater substitution of the less polar nitro radical for the hydroxyl radical, thus giving greater molecular cohesion. No method of differentiation between nitrocellulose pulps with respect to their graining characteristics was devised.
The formation of the spheres of dispersed lacquer, which are the balls of the Ball Powder process, was found to be a coagulation process and not the mere insolubility of the nitrocellulose in water as the solvent was evaporated, thus providing a means of controlling the coagulation by ordinary colloid chemistry methods (control of the zeta potential by the concentration of electrolyte in the water phase). Gels of different structure were made depending on the electrolyte.

This points out the basic difference in the behavior of Ball Powder over conventional smokeless powder, in that the former is coagulated as a network gel structure while the latter preserves its original micellar structure.

From the observations of the dispersion, it was apparent that with the experimental techniques attempted, it was not possible to determine the rate equation of the swelling of the nitrocellulose fibres in swelling agents. But certainly much more work is needed on the colloidal properties of nitrocellulose with particular reference to the zeta potential of cellulosics of varying nitrogen contents, the dipole
moment characteristics of nitrocellulose, and the effect of various polar swelling agents on nitrocellulose with particular emphasis on their polar moments.
II. ACKNOWLEDGMENTS

The author wishes to express his appreciation to Prof. Ernst A. Hauser for his supervision, suggestions, and guidance in the prosecution of this research.

Appreciation is also due the Western Cartridge Company of East Alton, Illinois, especially Mr. Fred Olsen and Mr. Milton Herzog, for their assistance in providing materials for the work and for their interest in the thesis.

Thanks are also due to Prof. Clifford B. Purves for his suggestions and to Mr. A. C. Watson for the generous use of his photographic facilities.
III. INTRODUCTION

In the manufacture of smokeless powder by the Ball Powder Process, a development of the Western Cartridge Company of East Alton, Illinois, an integral part of the processing is the dispersion of nitrocellulose after it is partially purified in some suitable solvent, the solvent used by them being ethyl acetate. In this step, for all intents the still fibrous nitrocellulose loses all of its fibre structure, after which the dispersed lacquer of nitrocellulose is carefully agitated to form spheres much in the manner of an emulsion. It is these spheres or balls which are solidified by distilling out the solvent that are the distinguishing characteristic of ball powder. This latter operation is referred to as "graining".

The present technique is to introduce the proper quantity of solvent to the cold suspension of nitrocellulose fibres in a closed vessel and then heating to 80°C. for an hour, agitating all the while. The lacquer so formed is purified by addition of the proper chemicals, washed with fresh water, and
allowed to rise to surface, as the lacquer is of lower density than the water phase surrounding it. This is called "creaming out". Following this is the graining step.

The dispersion of nitrocellulose presents two problems which form the basis of this thesis. One is the question of the proper time to be allowed for the dispersion, as the figure of one hour is purely arbitrary and is used because a satisfactory product can be obtained in this way. It would seem that there might be devised a mathematical equation which would describe the rate of gelation which in its ultimate limit would of course be complete dispersion. Very little was known about the dispersion mechanism itself, and thus it was necessary to study the general aspect of the problem.

The other problem has to do with the graining step. It was found in practice that there were certain nitrocellulose pulps which apparently were similar to all other pulps but which would not grain properly, giving a lacquer that would not form into spheres at all or else would form spheres that were too fine. The preliminary assumption was made that perhaps the non-graining characteristics were accountable
to incomplete dispersion, and that by studying the dispersion and evolving from that a comparative test, it would be possible to differentiate between the various pulps.

The purpose of this thesis is to investigate these two phases of the problem and make a general study of the mechanism of dispersion.
IV. SURVEY OF THE PREVIOUS LITERATURE

There was found, after a survey of the literature, that there was no pertinent information on either of the two problems stated in the introduction. This is understandable because the development of the Ball Powder Process was relatively recent and represents a wide divergence from the general practice of the explosives industry. There has been no quantitative work done on the swelling of nitrocellulose fibres as such.

1) Berl has published a few microphotographs of the swelling of nitrocellulose fibres in various solvents but fails to give any for the swelling in ethyl acetate, the solvent specifically concerned in this thesis. He merely makes note of the fact that nitrocellulose completely disperses in pure solvent at room temperature. The conclusion of his paper seems to be that the dispersing power of the solvents investigated is greater at the temperature of dry ice $-40^\circ$C., than at room temperature. His photographs are, on the whole, inconclusive.

1) E. Berl & W. Koerber; J.A.C.S. 61, 154 (1939).
A general description of the swelling of nitrocellulose as studied with a microscope was given by Mangenot and Raisoni\(^1\)). (See translation of paper in the Appendix). Their technique involved dyeing the fibres, noting that there was a filament-like structure on the surface of the fibre which did not absorb the dye and which seemed to indicate a spiral configuration of micellar arrangement which to some measure seemed to control the swelling.

There has been some literature on the swelling of sheet nitrocellulose with various solvents\(^2\)). However, one cannot extrapolate this information to fibrous structure because of the great differences of structure of the two and their entirely different dispersion characteristics. (For translation of film-making technique, see Appendix.)

1) G. Mangenot & M. Raison; Comptes Rendus \textbf{210}, 674 (1940).
V. PROCEDURE, RESULTS, AND DISCUSSION
A. RATE OF GELATION OF NITROCELLULOSE

The general procedure followed in this investigation was to add solvent of the proper concentration diluted with water or ethyl alcohol and to follow the swelling progressively with a microscope, taking pictures at regular time intervals of a geometrical progression, i.e., after 1 min., 2 min., 4 min., etc. These photographs were to be printed and the diameters of representative samples measured. The diameters would then be fitted into the general rate equation describing the swelling.

The following variables are thought to control the rate of swelling: the solvent used; the concentration of solvent; the polarity of the diluent; the time; diameter; temperature; pressure; history of the nitrocellulose up to that point; and the type of original fibre employed, that is, wood cellulose, cotton linters, ramie, etc. It was hoped that it would be possible to keep all but two of the above variables constant for one run, and by changing the variables, to determine all of the functions appearing in the general rate equation. The work carried out in this phase varied only the diameter against the
time. The other conditions were as follows: room temperature (25°C.); ethyl acetate as the solvent using a concentration of 35%; a diluent of either alcohol or water, emulsifying the water-ethyl acetate system first in a hand homogenizer; atmospheric pressure; and one sample of nitrocellulose, sample No. 54 or W-1169, which had a nitrogen content of 12.89% and had satisfactory graining characteristics.

Variations in procedure are given in the following sections.
1. FLUORESCENT MICROSCOPE

Procedure:

This was the original technique proposed. The fibres were dyed with fluorescent dyes using both Thioflavien-S and Malachite Green as described in the original Cambridge notes of F. Olsen and F. H. Olsen, 1938. To secure maximum fluorescent effect, the mixture of nitrocellulose and gelatinizing agent were held in a built up microscope slide of a thin glass ring of one millimeter thickness on a quartz slide to permit the passage of the ultra violet light. The slide was not cemented because it was necessary to clean it thoroughly and no satisfactory seal was discovered. This was then covered with a thin cover glass.

The microscope was a standard fluorescent microscope using a mercury arc as a source of ultra violet light, carefully filtering out the rest of the spectrum. A yellow 2X filter was put in the path after the cell to destroy the ultra violet light not fluoresced by the dye. A 9X objective was used for the most part.
Photographs were taken with a standard Leica attachment using Agfa Ultrapan Press film. The exposure time for ultra violet was found to be three minutes.

Thioflavien-S in the optimum dilution of one part per 10,000,000 produced a very weak fluorescence on the nitrocellulose after shaking vigorously. Furthermore, the fibres were dyed selectively, some fibres being not touched by the dye, and on the fibres that were dyed, there were spots which were much more highly fluorescent than the rest of the fibre. On the whole, the initial fibre diameters were quite uniform with the exception of the macerated fines produced in the Jordan beater or the hammermill (see photograph p. 16). The fluorescence was so weak that satisfactory photographs could not be taken.

Malachite Green was quite a bit better with an optimum dilution of one part per 100,000. However, photographing these fibres was still very unsatisfactory.

Discussion:
The purpose of the ultra violet technique was that as long as the large molecules of the dye remained
on the surface and thus were visible, it would mean that the fibre structure, though swollen, would still remain, as the large molecules would not diffuse into the mass. As soon as the fibre structure was disintegrated, the dye would disperse in the more or less uniform phase and fluorescence would disappear, as a field of pure dye at the concentrations used does not noticeably fluoresce.

The addition of the solvent did not affect the fluorescence.

On the whole, the fluorescence was not strong enough to be satisfactory and did not show representative samples, but only those whose peculiar surface condition caused preferential absorption of the dye. This method was abandoned partially because the exposure times were so long that appreciable swelling would have occurred and the initial two time periods would be lost.

Figure I shows a typical photograph of unswollen nitrocellulose fibres dyed with malachite green at the optimum dilution.

It is evident that the thickness of the observation cell limits the effectiveness of the fluorescence. Since a cell of appreciable thickness is necessary to reproduce reasonable dispersion conditions, this method is obviously inapplicable.
FIGURE I. Unswollen nitrocellulose, dyed with malachite green, dilution 1 p.p. 100,000, showing selective dyeing. (M-100x)

FIGURE II. Unswollen nitrocellulose, alcohol wet, wide latitude of fibre diameter. (M-100x)
2. NORMAL MICROSCOPY

Procedure: Ordinary light through a substage condenser system was used with a technique similar to that for the fluorescent technique. The diaphragm was stopped down all the way. Where noted, the photographs are semi-darkfield with some direct illumination, in order to emphasize the edges of the fibre.

Satisfactory photographs were taken with an exposure of fifteen seconds.

At first the solvent was emulsified with water, but the droplets of the emulsion obscured the fibres and therefore acetate diluted with alcohol was used instead. This raises the valid objection that the additional effect of the polar alcohol (all polar liquids seemingly have the property of swelling nitrocellulose to some extent) on the swelling. Nevertheless, the ethyl alcohol and ethyl acetate should give the same general swelling phenomenon as ethyl acetate alone.

Results and Discussion:
This gave a progressive series of photographs taken at time intervals of 1, 2, 4, 8 min., etc., representative of which are reproduced (Figs. III-V)

From these photographs, plus photographs of the original sample, alcohol wet (Fig. II) one can obtain a partial picture of the swelling process. Unfortunately,
FIGURE III. Partially swollen fibres after First Stage. (M-100x)

FIGURE IV. Second stage swelling. (M-100)
FIGURE V. Second stage swelling; fibre, upper left, has shrunk. (M-100x)

FIGURE VI. Longitudinally contracted fines, second stage. (M-100x)
it was found that ultimate dispersion did not occur before most of the solvent had evaporated from the cell. The photographs and observations show great variation in the fibre diameters at each time interval, although in the long fibres, swelling distinctly preserved the cylindrical shape of the fibre. With the wide latitude in the amount of swelling observable in the fibres at any one interval, it is dubious if the time interval is of any importance.

The microscope cell was not adequately sealed, and consequently the solvent was continuously evaporating, which changed the conditions. The photographs are indicative only of the general nature of the dispersion process.

Description of Swelling Normal Fibres

It was noticed that the swelling when the solvent first attacked the fibre was very rapid, producing an increase of from three to four times the original diameter (Fig. III). This was followed by a much slower period of uniform swelling parallel to the axis of the fibre (Fig. IV). After this point, most of the fibres did not swell any further, and as the ethyl acetate evaporated, actually began to shrink. (Fig. V, upper left corner). A few fibres did disperse completely. Here, the wall structure, which had been very distinct, was disrupted and the fragments of
fibre disintegrated radically from the most unreactive parts of the fibre.

**Fines**

The fines had an entirely different swelling pattern. At first, they swelled uniformly, but as the diameter of the gelled fibre approached the length, the fibre began to shrink longitudinally and swelled further radially (Fig. VI). When anisometric, the wall structure suddenly disappeared without rupture as in the case of the long fibres and the mass disintegrated radically as before.

**Mechanically Disrupted Fibres**

Those fibres with macerated ends after swelling normally for the first stage would then swell most at the ends, less in the middle. The ends would balloon out and curl back on the fibre. (Fig. VII).

**Coalescence**

If the suspension of nitrocellulose is too concentrated, there is a marked tendency for the fibres to coalesce with interpenetration of the outside gel casings (Fig. VIII). The gelled masses seemingly do
FIGURE VII. Swelling of fibrillated end. (M-180x)

FIGURE VIII. Interpenetration of coalesced fibres (M-100x)
not swell at all in the interior; gradually, one by one, the fibres on the outside are attacked and break away. Once coalesced, the fibre masses are seemingly more resistant than before to solvent action.

**Difficulties**

There are several difficulties with this method of study. As the solvent evaporates, (it would require a very elaborate piece of microscope equipment to prevent this), the concentration changes, thus introducing an unknown variable. Then, too, as the concentration changes, an unknown amount of shrinkage occurs which from observation was by no means uniformly distributed. It is doubtful that without any agitation that all of the fibres were even attacked by the solvent.

This makes any investigation of swelling of fibres not using a sealed cell of doubtful value; thus this method was discontinued and no further attempt was made to devise a piece of apparatus in which the swelling could be done on a microscope stage.

**Protective Coatings**

A further and far more significant difficulty was that the initial rapid swelling seemingly was
accompanied by a leeching out of the wall structure by the fresh solvent of the shorter molecules (or micelles if they be so arranged) which formed a dense film around the fibre. This is in accordance with the knowledge of cellulose; for it is known that the interstices of the long micelles forming the dense outer wall are filled with micelles of much shorter length and thus would be much more readily attacked. (Fig. IX).

This protective coating of high concentration of lacquer presents a great resistance to the diffusion of more ethyl acetate into the fibre mass. As the solvent evaporated, this casing shrunk proportionately more than the rest of the fibre and became even more protective.

**Importance of Agitation**

All of the above indicates the extreme importance of agitation during the dispersion process, which must be as vigorous as possible to break the shell of lacquer. It is quite possible that the dispersion time can be noticeably cut down by increasing the agitation.

This was a further reason for not continuing a wholly microscopic technique.
FIGURE IX. Diffusion front of nitrocellulose rich lacquer, showing leeching out action, first stage. (M-100x)

FIGURE XI. Stage 2. Uniform swelling (M-180x).
For the reasons noted before, mechanical agitation was added by placing in a test tube approximately 100 milligrams of wet nitrocellulose and a large excess of solvent of proper concentration (being 35% ethyl acetate, 65% benzene — otherwise the dispersion was so rapid that no differentiation in the different stages of the swelling could be made). The sample was put in a shaking machine for the standard time intervals. When viewed microscopically, the results were much more uniform than before.

Three Stage Swelling

It was found that the swelling fell into three distinct stages and that the difficulty of the lacquer coatings was largely avoided (before, it has been possible to see them because of the difference of index of refraction). The first stage was very rapid and probably was complete for most fibres after about thirty seconds of shaking. The diameter was increased from three to four times, in a few fibres as much as six times, but no fibres completely dispersing
(absence of any ruptured wall structures and disintegrating masses). A few fibres were resistant to the solvent, but on the whole, the swollen fibres were cylindrically swollen.

Second Stage

At the room temperature dispersions carried out, roughly half of the fibres stayed in this stage indefinitely. For the first three or four stages, swelling increased uniformly, but much more slowly than at first. After the fourth or fifth interval, very little swelling occurred. The fines were much more prone to dispersing completely.

Third State

A few fibres were noticed in the third stage of swelling, which occurred from the second interval onwards. With the long fibres, there was rupture of the wall and radial disintegration; with the very short ones (length being three or four times the original diameter), the same as before. Eventually, all of the very short fibres dispersed.
However, even though the shaking process was continued for as long as eighteen hours, swelling did not seem to have gone beyond about the fifth time interval. It was noticed that the final slurry contained about half the number of fibres as the original suspension. When held up to the light, it exhibited birefringence.

**Difficulties**

From the preceding, it is obvious that a room temperature dispersion at any concentration that will permit progressive following of the swelling will cover only part of the dispersion. Thus to get a picture of the complete process, it was necessary to duplicate industrial practice and disperse at an elevated temperature.

Noting that there is such a wide variety of fibres, even though the swelling is more or less uniform, it is doubtful if it will be possible to measure swelling quantitatively using some microscopic technique. It is necessary to take a sample containing a great number of fibres to even out the differences; to magnify enough to get fibres that were measurable meant that the field at one time had only
a few fibres. Only a small number of fibres could be suspended in order to avoid coalescence.
4. PRESSURE APPARATUS

A pressure bomb similar to the dispersion tank or graining still used in the plant was designed and constructed in an attempt to have a complete picture of the dispersion of nitrocellulose. The bomb had a capacity of 1800 cc. and insofar as possible, amounts proportionate to those used in the Ball Powder Process were used.

Description of Pressure Unit

The bomb was capable of withstanding high pressures of at least 200 p.s.i., and thus was proof against and pressure inside and correspondingly, temperature, up to about 130°C. Above this temperature the vapor pressure of the ethyl acetate is greater than the bomb will withstand and thus care must be taken to watch the equipment at all times while in operation. The bomb was a steel pipe fitted with two cast iron end caps and was jacketed with a double layer of Chromel A resistance windings back wound on the second layer to reduce inductance which might conceivably affect the dispersion of the highly
dipolar nitrocellulose. A tube projecting in the cell contained a copper constantin thermocouple carefully calibrated between 0° and 100°C. The temperature was controlled by a "Variac" variable inductance autotransformer unit which varied the voltage. It was found that the temperature inside the bomb could easily be maintained within one degree centigrade.

A series of voltage and amperage determinations showed that the inductance of about 12 ohms remained constant for any voltage which presumably means that the inductance has little or no effect on the nitrocellulose.

Two taps were provided in the top for filling and a tap about a third of the way from the bottom fitted with a valve for withdrawing samples. An agitator with three paddle type blades was fitted through a stuffing box. The agitation was quite uniform, as a series of samples withdrawn all had about the same thickness of slurry.

A great deal of difficulty was experienced in making the unit pressure proof.

A typical charge was about four grams of nitrocellulose, fifty grams of ethyl acetate, and 1200 cc. of water. The water was brought to a temperature of 60°, and then the nitrocellulose was added and finally the
ethyl acetate, emulsified with water. The bomb was quickly sealed up. This was brought to a temperature of eighty degrees, samples being taken continuously.

Results

The results were quite similar to the hand shaking with the exception that final dispersion was obtained.

The gelatinization was much more rapid than at room temperature, dispersion under some circumstances occurring at the end of six minutes. This is not to be compared with the industrial time of dispersion as there is much more solvent used.

When the apparatus was not leak-proof, the samples withdrawn were quite normal up to a certain point, and then suddenly no more fibres could be found. This point occurred rather shortly after the introduction of the ethyl acetate, being about twelve minutes. Upon opening the cell, a coagulum was found of nitrocellulose which had been deposited on all of the metal surfaces. This phenomenon will be discussed at length under the section: "The Graining Process".
5. OTHER METHODS

Other methods for studying the incorporation of the ethyl acetate into the nitrocellulose were suggested. Conductivity measurements would be very simple, but there are no conducting salts known which are exclusively soluble in organic liquids and not in water, which eliminates this method.

Quantitative measurements of swelling have been made by placing an excess of solvent over a known volume of nitrocellulose and measuring the increase of volume. But as the microscopic examination shows, coalescence occurs immediately and does not give at all similar conditions to the vigorous agitation during the dispersion.

Another suggestion was to put the fibres in a pan suspended from a delicate balance and measure the change of weight. It is just possible there would be a measurable decrease of weight corresponding to the material leached from the surface. Agitation is obviously the eliminating factor.

It was thought that it might be possible to measure the swelling quantitatively by soaking the nitrocellulose first in a chemical that will precipitate another
chemical to be dissolved in the ethyl acetate, and measuring the change of concentration in the liquid phase. This has the disadvantage that it really will be measuring the diffusion rate of the chemical and not the swelling of the fibre.

Furthermore, it is very difficult to make a direct determination of the amount of ethyl acetate used up in the swelling because of its limited miscibility with water and because the faster dispersing fibres when dispersed completely will release ethyl acetate, thus increasing the concentration instead of decreasing it.

**Conclusion**

Thus it is apparent that there is no satisfactory method for measuring the rate of swelling of nitrocellulose with the techniques now available. Although the degree of swelling has been correlated with the change of zeta potential for sheet nitrocellulose\(^1\), the extrapolation to nitrocellulose fibres would seem unwarranted because of the entirely different structures involved.

It is questionable whether the rate of swelling has very much meaning since the fibres themselves differ so markedly in their behavior. For this reason, no further work was done on the rate of swelling.

B. DIFFERENTIATION OF PULPS

The second general problem proposed in the introduction was the differentiation of various nitrocellulose pulps which had various graining characteristics. The difficulty is that some nitrocelluloses, apparently not at all different from other pulps, form undersized grains or imperfect spheres, which constitute an unsatisfactory product. The ballistic superiority of Ball Powder depending as it does on accurate control of grain size and perfect uniformity.

It was presupposed that this difference might be explained by a difference of molecular chain length, and that this difference would readily appear in the ease of dispersability in the standard solvent. In looking for a quick test to determine complete dispersion, the Tyndall beam effect for determining a colloidal system suggested itself. Some measure of the dispersability or the ease of dispersion would be given by the minimum concentration of ethyl acetate to cause complete dispersion as determined by the Tyndall beam.
1. DETERMINATION OF DISPERSION BY THE TYNDALL BEAM

Slurries of varying concentrations of pulp were observed in the Tyndall beam. The long fibres suspended in water would stay in suspension for a matter of several minutes and suspended themselves without shaking, giving proof of the strong negative electric charge on the surface of the fibres. This is quite remarkable when one considers that these electrostatic forces are acting over a distance of tens of microns.

The long fibres were clearly visible in the beam, giving sharp definition when about a tenth of a gram was added to 15 cc. of water.

Fibres partially swollen in solvent were also visible, but obviously lacking the definition accorded to the unswollen fibres.

Still further swelling, to the extent that the fibre structure has been broken down largely and the nuclei of nitrocellulose masses are disintegrating, appears as heavy beam with noticeable fine grain structure. This looks very much like a very fine emulsion. In the subsequent tests, this state will
be referred to as non-disperse, fibre structure disintegrated.

Just before complete dispersion, the grainy appearance of the beam disappears and becomes the ordinary white Tyndall beam, yet with lack of sharpness at the edges of the beam.

Complete dispersion gives the true beam with complete sharpness of the edges.
2. DISPERSABILITY IN ETHYL ACETATE–ALCOHOL

A standard procedure for dispersability was adopted, that being to add to one-tenth of a gram of alcohol wet nitrocellulose fifteen cc. of solvent of varying concentration. The test tube was shaken vigorously for twenty seconds and observed with a Tyndall beam.

Six samples were tested, three of them being of poor graining characteristics, two of them standard graining characteristics, and one also having good graining characteristics, but being of an entirely different type of pulp than the other five.

The results of the test very clearly differentiated the several pulps into three classes. The first is dispersion resistant (sample W1168) as it is non-disperse in a 50% ethyl acetate solution, whereas the rest disperse readily. This sample has bad graining characteristics.

The second class is the range of normal pulps, not dispersing in a range of concentrations from 30% to 40%, depending on the sample, and all three had good graining characteristics. Sample W1169 would

1) See Table I in Appendix
2) For characteristics of nitrocellulose, see Table III, Appendix
TABLE I

DISPERSBILITY OF VARIOUS NITROCELLULOSES
IN ETHYL ACETATE AND ALCOHOL OF VARYING
CONCENTRATIONS

D - dispersed completely in Tyndall beam
ND - not dispersed, fibre structure visible
NDF - not dispersed, but fibre structure has disappeared
F - a few fibres are apparently unattacked, but the majority have dispersed

Abstract of Results:

<table>
<thead>
<tr>
<th>% Ethyl Acetate</th>
<th>W1166 #54</th>
<th>W1167 #50</th>
<th>W1168 #5036</th>
<th>W1169 #5060</th>
<th>W1170 #3362</th>
<th>W1171 #52</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>D</td>
<td>F</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>70</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
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</tr>
<tr>
<td>50</td>
<td>D</td>
<td>D</td>
<td>ND</td>
<td>D</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>40</td>
<td>D</td>
<td>F</td>
<td>ND</td>
<td>D</td>
<td>ND</td>
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<td>ND</td>
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<td>F</td>
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<tr>
<td>20</td>
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<td>NDF</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
## TABLE II

**MINIMUM DISPERSABILITY CONCENTRATION AGAINST NITROGEN CONTENT**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Approximate minimum concentration of ethyl-acetate in alcohol to produce dispersion</th>
<th>Nitrogen Content</th>
<th>Viscosity (ctps.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. W1168</td>
<td>50%</td>
<td>13.42%</td>
<td>1.66</td>
</tr>
<tr>
<td>2. W1170</td>
<td>40</td>
<td>13.2</td>
<td>1.74</td>
</tr>
<tr>
<td>3. W1169</td>
<td>30</td>
<td>12.89</td>
<td>1.78</td>
</tr>
<tr>
<td>4. W1171</td>
<td>25</td>
<td>12.89</td>
<td>1.88</td>
</tr>
<tr>
<td>5. W1166</td>
<td>20</td>
<td>12.83</td>
<td>1.91</td>
</tr>
<tr>
<td>6. W1167</td>
<td>15</td>
<td>12.63</td>
<td>1.72</td>
</tr>
</tbody>
</table>
FIGURE X.
NITROGEN CONTENT vs. DISPERSABILITY

April, 1942.

F.W.C.
not disperse at 30% ethyl acetate; Sample W1170, not disperse at 40% ethyl acetate; and sample W1171, not disperse at 30% ethyl acetate. This latter sample, W1171, is not as sharply defined as the others, but is the sample taken from pulp of an entirely different nature, and therefore not rightly considered in this test. Of course, in all of the above, the nitrocellulose was completely dispersed in ethyl acetate concentrations greater than the figures mentioned.

The third class is too easily dispersed, not dispersing just at 20% solvent concentration. These are samples W1166 and W1167, both of which showed bad graining characteristics. It should be mentioned that sample W1167 showed a tendency even at much higher concentrations to have a very small number of fibres which were not dispersed.

Discussion

From the few samples tested, there would seem to be some correlation between the dispersability as determined by the minimum concentration of ethyl acetate in which the nitrocellulose will disperse completely and the graining characteristics. The nitrocellulose must not disperse too easily or be too dispersion resistant.
There is the consideration that the above results are to be expected directly from the nitrogen content, as higher nitrogen percentages generally make the pulp more dispersion resistant. A plot of the minimum ethyl acetate as against the nitrogen content (Fig. X) shows some divergence, but generally the points fall on a straight line. When more samples can be tested, the validity of this correlation can be better evaluated. It is entirely conceivable that the nitrogen content does directly influence the dispersion and graining characteristics. It would be very significant if such a correlation could be established.

Hypothesis

An explanation of the possible correlation can be made on the basis of polarity. The nitro group has a lower polar moment than the hydroxyl group which it displaces. The intensity of the dipole moment will of course determine the repulsive secondary valence forces set up in the individual nitrocellulose molecules and the distance through which they are effective as opposed to any attractive forces tending to cause agglomeration. The orientation of the molecules side by side is of course demanded by the dipole moment, which is cumulative with the length of the chain.
Dispersion Resistant

In the nitrocellulose of dispersion resistance and having the highest nitrogen content (cf. Table III, Appendix, p.67), the more strongly polar hydroxyl groups have been largely replaced by nitro groups, lowering the secondary valence molecular forces pertaining to resistance, and thus permitting the molecules to come closer together. This makes for a tighter micellar structure which one would expect to be dispersion resistant, since the attractive forces are independent of the polarity but the forces pertaining to resistance are directly so.

Too Easily Dispersed

Just the reverse of the preceding argument for the dispersion resistant nitrocellulose would seemingly apply to the nitrocellulose too easily dispersed. Here the lower nitrogen content means that fewer of the hydroxyl groups are substituted with nitro groups, making the result forces pertaining to resistance in the potential level theory of gel structure much greater. In the nitrocellulose fibre, the micellar structure is much looser, the attractive forces less
in control. One would expect that these would be too easily dispersed, which is indicated (see Fig. X) by the graph.

Normal Dispersion

Fibres with the intermediate dispersion characteristics also have intermediate nitrogen content. The micellar structure can be destroyed with corresponding ease.

Graining

The implication on the above hypothesis when applied to graining can be readily appreciated, and will be discussed in that section of the report, for in the graining operation, just the reverse of the above dispersion process takes place. Seemingly, the same energy potential considerations would apply.

Recommendations

It should be admitted that the above hypothesis is something of a speculation, but has the justification that it explains this and other phenomena with some success. First, however, it is necessary to determine the minimum concentrations of ethyl acetate for dispersion.
with much more accuracy than was carried out with
the runs given. Tests on more samples with differ-
et nitrogen contents is also important. The test
itself should be refined to give a more accurate
definition of colloidal dispersion than is possible
with the test stated, which is accurate to within
about 2cc. of solvent. An ultra microscopic examina-
tion would perhaps prove better were it not for the
elaborate preparation required by this method.

Variation with Viscosity:

There is the possibility that the dis-
persion is more a function of the viscosity than
of the nitrogen content. Comparing the minimum
concentration of ethyl acetate required for complete
dispersion with the viscosity, it can be seen that
there is an inverse correlation with one exception,
W1167. This can be substantiated by making tests on
nitrocelluloses of similar nitrogen contents but of
different viscosities.
3. DISPERSABILITY IN ETHYL ACETATE AND VARIOUS ORGANIC DILUENTS

There was raised the objection that the dispersability in ethyl acetate and alcohol may be influenced appreciably by the alcohol, which is polar and does swell cellulose and nitrocellulose. However, the pulp is initially wet with alcohol and presumably has swollen as much as it will in this reagent.

Benzene

Benzene, as a prototype of non-polar liquids, therefore was substituted for the alcohol. However, the benzene emulsified the alcohol and made observation in the Tyndall beam impossible.

Polar Diluents

One would expect that the polarity of the solvent would have a marked effect on the dispersion process, which is in accordance with the general rule that polar liquids disperse polar substances. It would also be desirable to use other polar diluents such as acetone, etc., which might give further correlation between the dispersability effects and the known polar moments of the various organic radicals appearing in the diluents.\textsuperscript{1)}

\textsuperscript{1)} cf. P. Debye, Dipole Moments.
C. DESCRIPTION OF THE DISPERSION PROCESS

From the observations made with the microscope and the various room temperature dispersions, there emerges a body of fact that should be reconciled to a consistent theory or explanation of the mechanism of swelling. It is evident that the swelling is extraordinarily complex.

The following facts appear, with regard to ethyl acetate as the swelling agent. First, at room temperature using the standard amount of ethyl acetate, the disperse state produced is of entirely different character from that produced at the elevated temperature of about 80° C. Secondly, there are apparently three distinct stages of swelling, as described in the preceding section. The temperature of the dispersion has a great deal of effect on the required time for dispersion. Furthermore, from the work of Berl and from observation, ethyl acetate is unique in its action as a solvent, which suggests some special mechanism for dispersion. The time for dispersion under proper conditions seems to be very short, occurring in well under five minutes in one observed run.
The Three Stage Dispersion:

As was described in the preceding section, the dispersion of nitrocellulose at elevated temperatures would seemingly fall into three distinct stages, the first, a rapid swelling, secondly, a uniform swelling parallel to the axis of the fibre, and finally, a rupture of the wall structure and subsequent disintegration of the fibre mass.

First Stage

The first stage is evidently a leeching out by the fresh lacquer of the shorter molecular chain length nitrocellulose on the surface of the fibre, forming a protective coating of lacquer that must be removed by mechanical agitation (Fig. IX). It is presumable that the surface molecules are more highly nitrated than the interior cellulose mass, being exposed to active nitration for the longest period of time. This results in a much lower di-polar moment from the lower polar moment of the nitro group over the hydroxyl groups replaced. This causes the surface material to be much more readily attacked in much the manner predicted by the hypothesis previously proposed. The first stage is obviously very short, occurring before diffusion of the solvent swells the interior of the fibre.
It is probable that the first stage does not involve the disruption of the micellar groups, for seemingly the short filler material to fill up the interstices of the oriented wall surface is not organized into micelles.

Second Stage:

Microphotographic technique has been applied to the benzylation of cellulose showing a remarkable layer structure of the cellulose fibre that is observed as striations in the fibre is sectioned longitudinally. These striations increase in thickness as the benzylation of the cellulose, accompanied by a consequent swelling of the fibre. The authors consider three mechanisms of this uniform type of swelling, which would correspond to the second stage of swelling described here. The first is a topochemical macroheterogeneous reaction, or layer to layer diffusion of the benzyl chloride; the second, a parmutoid-quasi homogeneous type of reaction in which a very high rate of diffusion causes all of the cellulose chains to be attacked at once; and the third is a strict micellar concept in which the reagent penetrates the

interstices of the micelles very rapidly and diffuses very slowly through the micelles. It could be considered loose terminology to speak of a penetration of the micelle by the benzyl chloride reagent if one considers the micelle to be a cohesive collection of oriented molecules based on some secondary valence attraction between like constituents—the so-called hydrogen bridging, and not some peculiar building unit made up of a shell protecting some amorphous material of lower molecular development. The results of their investigation eliminate the high diffusion rate explanation on the basis of the reaction vs. time curves and the photomicrographs show such heterogeneity of structure that they adopt the macroheterogeneous explanation.

**Macroheterogeneous Swelling:**

The mechanism they propose is that the reagent diffuses rapidly from layer to layer and then attacks the material in the planes surrounding the annular channels. They further observe the protective jelly of dispersed benzylolation of cellulose, there is nothing that corresponds the third stage of disintegration as the fibre structure is preserved.

Whatever of the three mechanisms may be responsible for the swelling, the swelling would necessarily be uniform
and parallel to the axis of the fibre as long as the fibre wall structure is preserved and the fibre is of reasonable length. The macroheterogeneous interpretation would emphasize that uniformity of swelling.

**Micellar Structure Preserved:**

In any event, it is doubtful if there is disruption of the micellar agglomerates during this second stage. None of the three proposals demand that the micelles dissociate. Instead, it is much more likely that the amorphous nitrocellulose around the micelles is dispersed into a lacquer that would tend to prevent and further dispersion until the actual disruption of the fibre wall and the introduction of fresh solvent. Unfortunately, there is no way in checking this later concept, as the so-called fresh solvent is already a thin lacquer resulting from the first stage.

Of course, all the foregoing assumes that the nitration of the cellulose stock does not disturb the micellar constitution of the original cellulose, a viewpoint that is borne out by H. Staudinger\(^1\), in which the term micellar as used by the author of this thesis must be translated as macromolecular, meaning an organization of molecules depending on energy considerations.

Photographic Representation:

The photographs representative of this second stage of swelling definitely indicate the uniformity of the parallel extension (Figs. XI - XXI). It can be seen that fibres of different length behave differently: disruption of the wall structure generally occurs at the fibrillated ends before in the center (Figs. XIV, XVIII); fines swell much more quickly than fibres with attendant contraction longitudinally (Fig. XV).

At the end of this stage, disruption of the wall properly begins (Figs. XIX - XXI). Swelling in all long fibres is not uniform, however (Fig. XVII).

Third Stage:

With the disruption of the fibre wall structure, there is a progressive disintegration of the partially swollen fibre mass extending radially from the center of a fibre mass. At this point, all uniform swelling stops and the micellar nitrocellulose is exposed to fresh solvent. It is at this point that the regular orientation of the micelles is broken down resulting in a random molecular arrangements. Depending on the concentration of the lacquer, and the temperature, it is possible for a very much extended structure to form.
Figures XXII–XXVIII show the progression of the dispersion during the third stage. After the disruption of the fibre walls, the fibres break up into more or less isometric masses (Fig. XXII–XXIV). These then disintegrate radially (Figs. XXV–XXVII) with the centers having the lowest concentration of solvent. However, some fibres are still dispersion resistant at this point, (Fig. XXVIII).

Once the micelles are dispersed into the solvent, they are themselves dispersed into a quasi-molecular state which probably associates itself as a network gel structure.

It should be emphasized that these photographs were taken of nitrocellulose treated at room temperature, and therefore the micellar structure is largely preserved throughout. However, this should in no way affect the photographic picturization of the stages of dispersion.

By emulsification of the lacquer with the water phase, and residual acid-and-water soluble impurity is of course removed. Here the residual water in the lacquer phase is removed by the Donnan equilibrium effect, following which the lacquer is allowed to cream out or coalesce into a uniform lacquer phase.
FIGURE XII. Stage 2, uniform swelling (M-180x).

FIGURE XIII. Stage 2, uniform swelling (M-180x).
FIGURE XIV. End swelling effect (M-180x).

FIGURE XV. Stage 2, extended parallel swelling, fines already largely dispersed (M-180x).
FIGURE XVI. Stage 2, contraction of fines (M-180x).

FIGURE XVII. Stage 2, non-uniformity of swelling (M-180x).
FIGURE XVIII. Stage 2, disintegration from end first; shorter pieces disperse more easily (M-180x).

FIGURE XIX. Stage 2, beginning of fibre wall disruption (M-180x)
FIGURE XX. Stage 2, beginning of wall disintegration (M-180x).

FIGURE XXI. Stage 2, disruption of the fibre wall (M-180x).
FIGURE XXII. Stage 3, disruption of fibre wall (M=180x).

FIGURE XXIII. Stage 3, start of radial dispersion (M=180x).
FIGURE XXIV. Stage 3, radial disintegration (M-180x).

FIGURE XXV. Stage 3, radial disintegration (M-180x).
FIGURE XXVI. Stage 3, radial dispersion (M-180x).

FIGURE XXVII. Stage 3, complete disintegration resistant fibre (M-180x).
FIGURE XXVIII. Resistant fibres (M-180x).

FIGURE XXIX. Film shrinkage pattern, no orientation (M-180x).
Uniqueness of Ethyl Acetate:

If we adopt the hypothesis of Berl\textsuperscript{1} in that the dispersion of nitrocellulose and other esters of cellulose in various solvents increases with a decrease in temperature, then we must conclude that the action of ethyl acetate is unique. He based his conclusions on observations at room temperature and at dry ice temperature. However, his conclusions are certainly invalid for ethyl acetate and nitrocellulose, because he notes merely that at both temperatures, one hundred milligrams completely disperse in two cc. of solvent. However, it cannot be said that the pulp disperses if one uses the word accurately, for actually a gel structure is set up and the micellar structure is completely preserved.

At the temperature of the dispersion, 80\textdegree{} C., ethyl acetate readily dissociates and has a vapor pressure of about an atmosphere and a half. It is suggested then that the mechanism of disruption of the actual micelles is that the ethyl acetate dissociates, resulting in a loose association between the acetate radicals and the free hydroxyl radicals. The similarity of

\textsuperscript{1} E. Berle & W. Koerber, J.A.C.S., 61, 134 (1939).
radicals then between ester (this term is used rather loosely here) and solvent permits final dispersion.

It would seem that if a catalyst could be found to increase the rate of hydrolysis of the ethyl acetate that the rate of dispersion of the nitrocellulose would be similarly increased. It was not possible to work on this phase of the problem with the equipment available, especially since the dispersion occurred so rapidly. Glass equipment, so that the process could be visually observed, would be helpful.

A Continuous Process:

From the several runs made in the bomb, it was obvious that the dispersion occurred in a very short time, under favorable conditions and a temperature of $80^\circ C.$ being about six minutes. It must be remembered that most of the six minutes were absorbed in bringing the materials up to the proper temperature. If the nitrocellulose and solvent suitably emulsified in water by some sort of homogenizer were introduced together at $80^\circ C.$, this time could be materially reduced.

One good method of accomplishing this is to heat the slurry of pulp and the solvent in coils of pipe around which steam is condensing, especially as the heat transfer coefficients for condensing steam are very favorable (in the order of 250 Btu. per hr. per sq. ft. per degree F.). The streams could be blended
at high velocity with violent agitation resulting from turbulent flow. Much more accurate work on the minimum time for dispersion plus the possibility of a catalyst for the ethyl acetate are needed first, however. In effect, this application would make the dispersion step continuous.

Carrying this principle even further, if as it seems, the graining is done under conditions of streamline flow, it might be possible to set up that streamline flow inside pipes, making this part of the process also continuous.

The possibilities of the continuous flow principle when applied to Ball Powder manufacture seem limitless. There is no reason to suppose that the nitration and washing stages could not also be carried out inside pipes. The continuous centrifuge is certainly an excellent application of this general technique.

**Shrinkage Patterns:**

Further evidence of the micellar dispersion of nitrocellulose fibres at room temperatures is given by the shrinkage pattern photomicrographs (Figs. XXIX to XXXII). These shrinkage patterns are formed by preparing a lacquer of ethyl acetate at room temperature,
FIGURE XXX. Film Shrinkage pattern, partial orientation (M-180x).

FIGURE XXXI. Film Shrinkage pattern, radially oriented (M-180x).
FIGURE XXXII. Film shrinkage pattern, parallel orientation (M-180x).
putting a drop of the lacquer on a drop of water, and then letting the solvent evaporate from the surface.

Three distinct types of patterns are formed. One is a blanket like formation showing no preferential orientation in the surface film (Fig. XXIX). The second type (Fig. XXX, XXXI) shows some parallel orientation in the film with radiating lines, and is caused by one point of the film becoming anchored.

A very clear indication of the micellar arrangement is given by the photographs of a film under tension Fig. XXXII, in which there is a very strong and marked orientation. Here it is believed that the tension occurs along the parallel horizontal lines, causing the micelles to orient themselves in thin lines. The folds at right angles are the preferential orientation of the film not under tension and would correspond to the partially oriented shrinkage pattern of the above (Fig. XXXI). The shortest distance between the parallel tension lines approximates ten molecular lengths.

With this very marked patterning, it is inconceivable that the orientation could be of molecularly dispersed nitrocellulose, but must necessarily be of
some much larger building unit, which would be the fundamental micelle of the cellulose fibre. It has been readily accepted and well substantiated that the esterification of natural cellulose fibres does not destroy the micellar constitution of the cellulose.

This is not to be confused with the dispersion of nitrocellulose in the minimum concentration of ethyl acetate, the test described in Section B, which test being carried out under entirely different conditions and with a much greater solvent concentration. In addition, it is these micellar associations of molecules which give the strongly colloidal polar properties. This does not necessarily imply that the individual micelles themselves have been disrupted, but concerns only the forces between colloidal micelles.
D. THE GRAINING STAGE

After the dispersion with the ethyl acetate and water emulsion, the lacquer formed is allowed to settle to the top of the tank and "cream out". It was found by Professor E. A. Hauser that this creaming out stage was very important to the successful formation of the spheres of powder\(^1\). When this step was not included, the lacquer did not coalesce and the grains formed were irregular but of satisfactory weight.

Following the creaming out is the graining stage in which the lacquer is agitated carefully and partially emulsified with the water phase. The solvent is evaporated from the spherical drops of lacquer and the balls gradually harden.

It was found from observations on many of the runs in the pressure bomb during the study of the swelling that the graining of nitrocellulose is distinctly a coagulation phenomenon and not merely a deplasticization of the gel structure by evaporation of the solvent. This was further substantiated when coagulua were produced in a system in which there was more than enough solvent present to preserve the lacquer phase.

As the solvent is evaporated it may be reasoned that the completely dispersed nitrocellulose (that is, no longer having any micellar structure) suffers a reduction of zeta potential due to loss of associated

1) E. A. Hauser; Preliminary Report to Western Cartridge Company, Graining of Nitrocellulose.
acetate until the coagulation or isoelectric point on
the colloid potential curves is reached resulting in a
coagulum of lowest energy level; Were it possible to
make accurate measurements, it would be found that this
particular step would liberate heat.

Since the graining step is simply one of colloidal
coaulation, it would seem possible that one could control
the properties of the gel structure formed by the presence
of proper electrolytes in the organo phase of the system.
With this in mind, tri-valent ferric ions were added to
the system and the solvent was evaporated in a glass
system so the gel structure could be observed. The be-
havior was entirely different from the gel formed when
there were no positive ions present. A much more extended
gel structure formed and seemed to have much more stability
with the addition of ferric ions. The difference between
the two can easily be deduced from the energy potential
curves, which this time must have a minimum below the
iso-electric point. When the second iso-electric point
is reached, the associated electrokinetic field is of
greater diameter, which indicates a method for increasing
the grain size. There is no attendant difficulty in
adding ferric ions to the organic phase because of the
limited miscibility between water and ethyl acetate.
Probably far more important than the above effect is that of bridging of the molecules by means of the multivalent positive ions. Undoubtedly during the nitration there will have been some degree of oxidation of the remaining hydroxyl groups to acid groups. It is these acid groups which could be bridged from molecule to adjacent molecule by the metallic ions.

Thus there are two effects tending to influence the grain size, one the presence of ions which control the energy potential characteristics (that is, multivalent positive ions causing coagulation at the second isoelectric point, where as monovalent ions cause coagulation at the first isoelectric point), and the cross bridging by either divalent or trivalent positive ions. Of the two effects, the latter, cross bridging, is probably the more important.

For the above reason, the addition of sodium sulphate electrolyte, which has been standard practice, (presumably for dehydration according to the Donnan equilibrium effect) should have little effect on the grain size, and certainly would tend to keep grain size at a minimum.

Referring to the preliminary report on graining by Professor E. A. Hauser¹, there is correlation between this concept and his conclusions. He stresses the
importance of keeping the temperature of solvent evaporation low in order that the surface of the grain may not be too rapidly desolvated. Should this happen, shrinkage and an irregular shape will result. There can possibly be an additional reason for lowering the temperature; the heat liberated during the coagulation, consequent from a lowering of the energy potential level, would also tend to desolvate the surface excessively.

Many of the coagula produced with the addition of ferric ions were large, and it was noticed that the surface was hard and tough, the interior soft and still quite plastic. The coagula were rubbery in aspect, which is to be expected since this is a reproduction on a highly macroscopic scale of the factors responsible for the properties of rubber.

Conclusions:

From the above discussion, it is apparent that the grain size and the gel structure can be directly controlled by the addition of multivalent positive ions. This is implied by the fact that the graining step is distinctly a colloidal coagulation phenomenon and not merely a desolvation of the lacquer on evaporation.

1) E. A. Hauser, Preliminary Report to the Western Cartridge Company on Graining of Nitrocellulose.
Furthermore, it would seem desirable to lower the temperature during desolvation or the hardening step, especially with the additional heat effect from the coagulation which occurs when the solvent concentration reaches a certain point.

Recommendations:

It is recommended that a series of runs be made using a laboratory graining apparatus which is a replica of the plant apparatus in which various concentrations of bi- and trivalent positive ions are incorporated into the organic phase.
E. DISPERSION IN THE BALL POWDER PROCESS
CONTRASTED WITH THE CONVENTIONAL PROCESS

From the preceding discussion, it is possible to indicate the basic colloidal differences between the Ball Powder process and the so-called Conventional Powder process.

Conventional Process:

During the dehydrating stage, the effect of the alcohol is merely to swell the fibres and to cause partial coalescence.

The following blocking presses and the macaroni press probably break down the fibre structure completely in a roughly mechanical manner, but do not destroy the micellar structure of the original fibre.

The mechanical working then causes the plasticized mass to coalesce into a reasonably homogeneous mass.

Ball Powder Process:

The Ball Powder process, on the other hand, completely disperses the nitrocellulose beyond the micellar state. In the subsequent graining stage, the progressive desolvation sets up a network gel structure which is highly electrocratic and which coagulates to the grains of ball powder.

Since a much higher degree of dispersion is accomplished, one would expect greater uniformity and homogeneity of final product.
VI. SUMMARIZED CONCLUSIONS

Considering each of the sections discussed in part V, it is possible to list the following summarized conclusions:

A. Rate of Gelation of Nitrocellulose

1. Following the progress of dispersion with a fluorescent microscope technique does not give an adequate picture.

2. Using a straight microscopic method, some indication of the dispersion is given, but the picture is distorted because of lack of agitation.

3. Mechanical agitation is a distinct improvement, but with the dilution of solvent used, complete dispersion was not obtained.

4. Heating in a pressure bomb resulted in final dispersion in considerably shorter time than the one hour allowed industrially, and was more in the order of a couple of minutes.

5. With the experimental methods available, it does not seem possible to determine a rate equation describing swelling or gelation. Considering the wide variations in individual fibres, the significance of such a rate equation is open to question.
B. Differentiation of Pulps

1. A simple, but rough test was devised for indicating complete dispersion. This test does not differentiate between micellar and quasi-molecular dispersion.

2. A correlation was established between the dispersability of a pulp and its nitrogen content. More thorough testing would be desirable.

3. An explanation of the above correlation was made on the basis of a consideration of the change of polarity with changing nitrogen content.

C. Description of the Dispersion Process.

1. The dispersion process may be conveniently considered to take place in three stages.

2. The first stage involves a rapid, parallel (to the longitudinal axis) swelling accompanied by a leeching out lower organized surface material which forms a protective film around the fibre.

3. The second stage is a much slower, parallel, and largely uniform swelling of the fibre.

4. The third stage involves disruption of the fibre wall and structure to form nearly isometric fibre masses which disintegrate radially.

5. Room temperature dispersion apparently yields micellar dispersion only.
6. Dispersion at an elevated temperature apparently results in a quasi-molecular state of dispersion which constitutes itself as a loose network gel structure at sufficient concentration.

7. Photographs showing marked preferential orientation of shrunken films give added indication of the micellar constitution of a room temperature dispersion.

8. The mechanism of the dispersion was indicated, in that it might be due to loose addition compounds with the free hydroxyl groups of dissociated ethyl acetate.

9. The possibility of a continuous process over batch for the dispersion of nitrocellulose was discussed.

D. The Graining Stage

1. Formation of the balls of powder was shown to be a colloidal process of coagulation and not mere desolvation as the solvent is evaporated.

2. Gels of different extension were prepared by the addition of suitable multi-valent positive ions to the organic phase.

3. A method of controlling the graining along colloidal lines was suggested.
E. Dispersion in the Ball Powder Process Contrasted with the Conventional Process

1. In the Ball Powder Process, there is a quasi-molecular dispersion of the nitrocellulose, while in the conventional powder making process, there is merely coalescence of the fibres.

2. The formation of grains in the conventional process is a question of deplasticization, whereas in the Ball Powder Process, the balls are the result of coagulation.
VII. RECOMMENDATIONS

It is recommended that:

1. Further work on the rate equation expressing dispersion be discontinued.

2. A catalyst for the hydrolysis of the ethyl acetate be investigated.

3. A consideration be made of the redesign of the dispersion step to introduce both reactants at the elevated temperature in order to reduce the time for complete dispersion.

4. A more extensive correlation between the nitrogen content and the minimum concentration of ethyl acetate for dispersion should be made. A correlation should be attempted between the electrokinetic properties of colloids (zeta potential, polarity and dipole moment) and the nitrogen content. The influence of viscosity should be checked.

5. Further work should be done on the effect of the electrolyte on the resultant coagulum produced in the graining operation.

6. A carefully designed micro-still be constructed for the pursuance of the investigation.
APPENDIX
<table>
<thead>
<tr>
<th>Number</th>
<th>Pulp</th>
<th>Sour Boil</th>
<th>Beating</th>
<th>Hoeppler Viscosity (ctps.)</th>
<th>Acetone Solubility</th>
<th>Ether Alcohol Solubility</th>
<th>Nitroglycerin</th>
<th>Combined Acidity</th>
<th>H2SO4</th>
<th>Ash</th>
<th>Finess</th>
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<tbody>
<tr>
<td>50</td>
<td>Kraft</td>
<td>No boiling</td>
<td>1 pass thru Dixie .020&quot; screen</td>
<td>1.91</td>
<td>99.89%</td>
<td>93.38%</td>
<td>12.33%</td>
<td>0.34%</td>
<td>0.48%</td>
<td></td>
<td>70cc</td>
</tr>
<tr>
<td>52</td>
<td>Purayonier</td>
<td>10 hours</td>
<td>&quot;</td>
<td>1.88</td>
<td>99.91%</td>
<td>98.63%</td>
<td>12.89%</td>
<td>0.14%</td>
<td>0.21%</td>
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<tr>
<td>54</td>
<td>Kraft</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1.78</td>
<td>99.95%</td>
<td>79.22%</td>
<td>12.89%</td>
<td>0.17%</td>
<td>0.19%</td>
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<tr>
<td>OP. #3362</td>
<td>Precut Cellulose</td>
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<td></td>
<td>1.74</td>
<td></td>
<td></td>
<td></td>
<td>13.2</td>
<td></td>
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<tr>
<td>Lot #5036 Hercules Pyrocotton</td>
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<td></td>
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<td>99%+</td>
<td>99%+</td>
<td>12.63%</td>
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<tr>
<td>Lot #5060 Hercules Guncotton</td>
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<td>1.66</td>
<td>Trace</td>
<td>6.56%</td>
<td>13.42%</td>
<td></td>
<td></td>
<td></td>
<td>82cc</td>
</tr>
</tbody>
</table>

* Data furnished by Western Cartridge Company

** 0.5 grams in 100 grams of 95% acetone
V. THE DETERMINATION OF THE DEGREE OF 1) SWELLING OF PREPARED NITROCELLULOSE IN VARIOUS ORGANIC SOLVENTS

As the prepared nitrocellulose 2) placed in a 10% concentration of acetone dissolved, the solution was poured on a glass plate suspended on mercury, and the acetone was evaporated. The whole was placed in a dessicator over P_2O_5 under vacuum for four weeks so that the small bubbles of air in the system could be removed. Then the plate-like sample, so formed about 2 mm. thick, was, after being thoroughly dried, placed in contact with 20 cc. of the fresh solvent and allowed to stand. At various time intervals with each of the various swelling agents, the sample was pressed between two filter papers and then carefully weighed. The degree of swelling was expressed as grams of solvent per 100 g. of dried sample.


2) Since the state of the "prepared nitrocellulose" is not known, this imposes a limitation to the analogy of swelling of fibres.
CONCERNING THE MORPHOLOGICAL CHARACTERISTICS
OF THE GELATINISATION OF THE CELLULOSE NITRATE
MEMBRANES 1)

By Georges Mangenot and
Madeleine Raison

We have followed, under the microscope,
the action, in various gelatinizing agents
(nitroglycerine, methyl nitrate, nitrate of diethylene
glycol, cyclopentanone), of the filaments or fibres
of di- or tri-nitrate cellulose 2) prepared from
cotton and ramie: these dispersion agents swell
the nitrated membranes, then agglomerating them in
a gel more or less homogeneous 3) having the consist-
ency of a gelatin or agar gel 4) finally dissolving
them. Pure methyl nitrate or pure cyclopentanone
act very vigorously, nitroglycerine very slowly, but
nitrate of diethylene glycol, or better still, cyclo-
pentanone diluted with hexane, produces a "manageable"
dispersion, nevertheless rapid enough so that one can
observe the images during the course of the dispersion,
which is of great interest. The study is made easier

1) Comptes Rendus, 210, 674 (1940).
2) The dinitrated fibres are attacked by all of the
gelatinizing agents; the trinitrate, only by the
cyclopentanone. (author's comment)
3) In actuality not homogeneous.
4) This is collaborative.
by dyeing the nitrocellulose gel with a hydrophobic colour (i.e., Soudan red, Soudan black, B.Z.L. blue, or indophenol blue). These colours are very soluble in the nitrocellulose gelatinizing agents. They permit, for example, superb colouring of dynamites, the microscopic drops (spheres) of nitroglycerine having vivid colouration in the interstices of the diatoms of the Kieselguhr. One notices that, if the nitrocellulose gel is coloured by these substances, the colour is not "retained" by the fibres or filaments not gelatinizing; it seems that the large molecules of the dye cannot penetrate the dense structure formed by the micelles of the membrane configuration.

The fibres of cotton, di- or tri-nitrate, treated by the diluted cyclopentanone, dissolve without appreciable swelling; in the measure that the nitrocellulose of the fibres passes into the gel state, one can detect on the surface of the fibres a delicate system of configurations in the form of rings and spirals; since some of these configurations appear on the surface of the fibre in the way of the dispersion without swelling, one notices the diversity of their disposition: rings more or less close together, very
fine or very marked, spirals more or less held at
the loose turns or ridges, with all the possible
intermediaries. One can interpret these formations
as the evidence of the existence, on the surface of
the fibre, of a circular binding, irregularly placed,
consisting of a system of very fine fibrils; the
fibre, entirely empty of soluble nitrocellulose (in
the subsequent dispersion), presents, therefore, in
the regions where the configurations are least dense,
a great resemblance to a spiral or ring-like lignous
structure. These fibrils can elsewhere roll them-
theselves out into long waving filaments or settle out,
forming the refractive rings; it is frequent that the
fibre should be sectioned: where the presence, in the
preparation, of the cylinders comes from spiral or
ring-shaped wall structure. In the axis of each
dissolved fibre, there is, generally, a trace of a
cellular cavity, in the form of a double series of
fine insoluble lumps. The nitrate of ethylene glycol
forms first, around each fibre of dinitrated cotton,
a thin layer of gel; then the fibre, disjointing
itself in needle-like fragments, rapidly dissolves,
becoming a gelatinous cylinder around which the fibrils
seemingly unroll like thread from a bobbin; but the
process of swelling permits, here, more usually a swelling procedure, very marked in certain points, and then a breaking of the gel into many fragments with the fibrillar parts settling out: these configurations are less vivid than those produced with cyclopentanone.

(There follows a description of the action on ramie.)

The superficial fibrillar system, spiral or ring-like, of the cotton fibres is certainly to be expected: such observers as Schlotmann, Griffionen, have observed on the surface of the fibre unattacked fragments when acted upon by aqueous dispersing agents (Schweitzer's reagent, sulphuric, caustic, zinc chloride). We have verified the validity of their observations by following the action of Schweitzer's reagent on cotton; but if the effects produced by the aqueous dispersants on natural cotton and by the hydrophobic dispersing agents on nitrocellulose are comparable, this stirs up a very difficult problem: certain of the agents do not hydrolyze, ¹) certain of the others, using the proper dilution, do

¹) Probably means hydrated.
²) This alone would speak of a necessary difference of behavior.
not cause the same degree of swelling, even with the most careful measurements. The system of the superficial fibrils, ring-like or spiral, of cotton gives evidence of the tubular structure of the membrane of primary pectic cellulose (comprising in essence the non-nitratable cellulose) of the fibre; the evident resemblance between this system of fibrils and ring and spiral configurations of lignins does not seem to be fortuitous: the disposition of these configurations explains the existence, in the primary cell walls of other types of cells, keeping in mind the differentiation, of a micellar structure similarly disposed. Finally, the absence of circular fibrils in the dinitrated fibres of ramie subject to the action of a gelatinizing agent, should be in accord with the absence, around the degummed fibres, of a primary wall; they having only secondary wall structures of micelles oriented parallel to the axis of the fibre.
LITERATURE REFERENCES:

2. P. Debye, Dipole Moments.