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John J. O'Neill Jr.

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CELLULOSE PELLETS

BY

JOHN J. O'NEILL, Jr.

A

THESIS

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Approved by W. T. Schrenk
Professor of Chemical Engineering

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The author wishes to acknowledge also the contributions of Mr. E. P. Reichardt, my colleague in this development.

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Cellulose Pellets

I. INTRODUCTION

This thesis describes the development of a new process for the manufacture of spherical particles of cellulose, regenerated from cellulose zanthate.

An electric equipment manufacturing company advised the author's company(1) that it had developed a device that required uniform spheres of regenerated cellulose having a diameter of about 75 to 100 mils. This company reported that it had developed a process for the manufacture of the cellulose particles but that the spheres produced by the process were not uniformly spherical. The equipment manufacturer considered that the functioning of the new device could be improved if the cellulose particles could be made more nearly spherical.

The contact was made because the author's company developed and owned the Ball powder process.(2) It was thought that if nitrocellulose could be made into nearly perfect

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(1) Western Cartridge Company, Division of Olin Industries, Inc., East Alton, Illinois

(2) Olive, T. Ball Powder. Chemical Engineering, Volume 53, pp. 92-96, December, 1946.

spheres by the techniques used in the manufacture of Ball powder, then cellulose zanthate could probably be formed into spheres by the same technique.

Attempts were made to regenerate cellulose zanthate in the shape of spheres using the well known Ball powder techniques, however, these procedures proved to be unsuited for the cellulose system and an entirely new procedure was developed, as described in the following pages.

II. LITERATURE SURVEY

General

The Ball powder process(3) which was selected as a basis for the new development is used to form dense, spherical particles of nitrocellulose. This form of the cellulose ester is usable as a propellant charge for small arms ammunition.

The procedure followed is to add nitrocellulose to a large, agitator equipped, tank containing about ten parts of water for each part of nitrocellulose. A water immiscible solvent, such as ethyl acetate, is then added to the charge to dissolve the nitrocellulose. In about one hour the nitrocellulose is fairly well dispersed in the solvent and, in addition, a quantity of water is emulsified in the nitrocellulose-solvent lacquer. When the solution is complete a protective colloid is added to the water phase. The presence of this material prevents a coalescence of the nitrocellulose lacquer as parts are separated from the mass of lacquer by the agitator. Protective colloids are so effective in preventing coalescence in the system that usually within 30 minutes the mass of lacquer, which, prior to the addition of the protective material, existed in the form of a few large masses of dough-like material, is dis-

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(3) Olive, op. cit., pp. 92-96

persed into millions of small globules. The suspension of these globules of lacquer in the water phase by the agitation of the system causes the particles to become spherical. This mechanism proceeds because of the interfacial tension of the system, and the fact that the viscosity of the lacquer is sufficiently low to permit the shape of the globules to become adjusted under the influence of the exerted pressures. The water emulsified in the globules is removed from the lacquer by adding approximately 2 per cent salt (sodium sulphate) to the water phase. The dissolved salt exerts sufficient osmotic pressure to extract the water from the particles. The solvent is then removed from the particles by distillation while they are still suspended in the water. The nitrocellulose from which the solvent is removed is in the form of dense, hard, spherical particles of various sizes. Under ordinary conditions the majority of the particles have a diameter greater than 6 mils while the larger particles seldom have a diameter larger than 30 mils.

Cellulose zanthate,(4) which is commonly known as viscose, is a soluble form of cellulose that can be regenerated in desirable forms.

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(4) Reinthaler, F. and Rowe, F.M. Artificial Silk. N. Y., Van Nostrand, 1928. pp. 48-100.

Viscose is made by reacting cellulose with sodium hydroxide to form sodium cellulose which is then reacted with carbon disulphide to form cellulose zanthate. The latter material is dissolved in 3% sodium hydroxide to form viscose syrup. The syrup is aged so that it can be regenerated under uniform conditions after spinning to form yarn or sheeting to form cellophane. Regeneration is usually accomplished by passing the spun syrup through a coagulating bath of sulphuric acid and sodium sulphate. Many acids and salts are effective coagulators of viscose. The regeneration process converts the cellulose zanthate to cellulose releasing the caustic and carbon disulphide.

III. SPECIFICATIONS FOR PRODUCT

At the start of the project the following specifications were established for the cellulose particles:

1. Cellulose Parent Material

   Conventional, commercial, aqueous viscose syrup of 1.12 sp. gr. and of the following typical composition:

   5-7.5% cellulose
   6-7% caustic soda
   2% carbon bisulphide in combination

2. Ball quality

   Average Diameter................90± 5 mils

   Roundness
   Dia. Ratio Major to Minor....1.20 or less
   1.05 or less preferably

   Sp. Gravity - order of.........1.5 to 1.6

   Bulk Density - order of........0.94 to 0.98

   Number of pieces per pound-
   order of........... 42,000 to 46,000

   Percent loss 42 hours @ 100 to 110°C moisture - order of......................5 to 8

   Surface...........Reasonably smooth. Free of nibs, or tails and excessive wrinkles.

   Color.............Light to medium amber, translucent and clear.

   Chemical..........Washed free of electrolyte to retain essentially no more impurities than those present in distilled or good grade city water. Ash order of 0.12% or less. Residual refractory oxides order of 0.01% or less

IV. PRELIMINARY EXPERIMENTS

The project to produce spherical particles of regenerated cellulose was started with a plan to substitute viscose syrup for the nitrocellulose-solvent lacquer in the ball powder system. A further change that was planned was to substitute a liquid immiscible with the viscose for the water normally used in the ball powder process. Benzene and carbontetrachloride and solutions of those materials were selected as immiscible liquids to be tested in the preliminary experiments.

Cellulose zanthate was prepared as taught by the literature(5) in laboratory equipment and suspended by agitation in solutions of benzene and carbontetrachloride to form spherical particles of cellulose zanthate. This approach proved to be unsatisfactory as the globules of cellulosic material entrapped the immiscible liquid, to some extent, thus producing particles that would not meet the density specification.

The fact that drops of cellulose zanthate, falling through the air could form into spheres was known to the author as this was the method used by the equipment manufacturer. The manufacturer had reported that spherical droplets formed while falling through air but that on re-

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(5) Reinthaler, op. cit., pp. 48-100

generation and drying they became deformed. The author reasoned that if a more perfect sphere could be made by an improved dropping method and if these spherical particles could be suspended in a liquid phase during regeneration the forces tending to deform the particles would be minimized. It was on this basis that the plan of attack was changed for experiment No. 7. This conception was successfully reduced to practice as described in the following pages and resulted in a process which consists of dropping viscose particles through air into a solution of carbontetrachloride and benzene of such a density that the particles slowly settle. The particles then fall through a liquid interface and into a salt solution that causes the particles to regenerate to form cellulose. While the particles are regenerating they are kept suspended in the salt solution by gentle agitation. Only after regeneration is substantially complete are the particles removed from the agitated salt solution.

A complete report of the preliminary experiments follows:

Experiment No. 1

Cellulose zanthate was prepared in the following manner:

Soda cellulose was prepared in several small batches by adding 5.68 parts of 17% to 18% sodium hydroxide to one part of air dry, precut cellulose. The soda cellulose was then aged for 24 to 48 hours. The aged material was then pressed to extract the excess caustic. The pressed material contained 4 to 5 parts caustic per part of cellulose. Small batches of this material were then zanthated by mixing it in a small W-P mixer with from 15% to 40% carbon bisulphide, based on the weight of the original cellulose. The mixture was kneeded for 4 to 6 hours and the zanthate so produced, ripened for 12 hours.

The zanthate was then prepared in four separate lots of different viscosities by adding a 3% to 5% solution of sodium hydroxide to the zanthate in the following proportions: 2 parts caustic - 1 part zanthate; 3 parts caustic-1 part zanthate; 4 parts caustic - 1 part zanthate; and 5 parts caustic - 1 part zanthate.

The first ball forming experiment was made with the above viscose by adding the material to a beaker of carbon-tetrachloride and stirring. The density difference was so great that the viscose scummed on the surface despite the stirring. Next, benzene was tried as a non-solvent medium, however, the density of this liquid was too low and the viscose coalesced at the bottom of the beaker.

Experiment No. 2

The specific gravity of the viscose was found to be 1.175, therefore, in order to provide a suspending medium of appropriate density a mixture of benzene and carbon tetrachloride having a specific gravity of 1.176 was prepared.

Viscose which had been made up with the five parts caustic was stirred in the benzene-carbontetrachloride and spherical particles of the cellulose were obtained. These particles were regenerated by transferring a few to 17% acetic acid. In another experiment acetic acid was added to the two phase system, however, this caused all of the viscose to coalesce.

Experiment No. 3

Experiment No. 2 was repeated using other regenerating agents. Viscose made with the five parts of caustic per part of cellulose zanthate was used. One hundred fifty grams of this solution was added to 1500cc of the benzene-CCl_4 having a specific gravity of 1.176. The materials were stirred with a laboratory mixer and the cellulose solution became dispersed in the form of spheres.

Grains of viscose were transferred to regenerating baths of 17% acetic acid, sulphuric acid of different concentrations, concentrated sodium chloride, and concentrated sodium sulphate. The sodium sulphate solution appeared to gelatinize the viscose. The sodium chloride regenerated more rapidly, but still was considered to be rather slow. The sulphuric acid was a very rapid coagulator, however, the cellulose particles were coalesced in the acid solutions. The acetic acid appeared to regenerate the viscose at a very desirable rate. The balls resulting from these experiments were too small. The experiment was then made with more viscous cellulose solution (4 parts caustic, one part cellulose zanthate). Concentrated acetic acid was used and balls having a diameter as large as 180 mils resulted.

Experiment No. 4

The last experiment was repeated and on the following two days the pellets from these experiments were dried. It was found that the cellulose particles contained entrapped carbon tetrachloride-benzene (shaping bath liquid). In some cases the cellulose was regenerated so that only a hollow shell surrounding a droplet of the shaping bath resulted.

Experiment No. 5

The literature reported that viscose solutions could be coagulated by heat as well as by the action of salts or acids(6). An experiment was therefore performed in which the cellulose zanthate syrup was dispersed in the shaping solution to form spheres and then coagulation was achieved by means of heat rather than by the salts and acids used in previous experiments.

Viscose made with 4 to 5 parts caustic was deaereated by placing 220 grams in a bell jar and evacuating until most

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(6) F. Reinthaler, op. cit. p. 51

of the air entrapped had been removed from the syrup. This quantity of syrup was then placed in a three necked, three liter flask containing 2000cc of the shaping bath solution having a specific gravity of 1.175 at 25°C. room temperature.

The ball formation took place between 8:45 P.M. and 9:20 P.M. at a temperature of 25°C.; at 9:25 P.M. the temperature was raised to 60°C. The temperature was then allowed to rise slowly and at 10:00 P.M. the temperature was at 70.5°C. and the shaping solution began to reflux. Refluxing was continued all night and at 8:00 A.M. the next morning the balls had been regenerated. This opened the possibility of using heat alone as the coagulant, however, the grains were not satisfactory because of entrapped solvent.

Experiment No. 6

Viscose syrup made with 4 parts caustic was used for the experiment on this day in which 510 grams of the syrup was added to four liters of shaping bath having a specific gravity of 1.175 at 25°C. After the balls had formed the entire mass was added slowly to one liter of glacial acetic acid. The new mixture was then agitated for 8 hours. The balls at that time were large, spherical, however, they contained entrapped shaping bath.

Experiment No. 7

The experiments recorded above establish that viscose syrup could be formed into spherical particles and that the balls could be regenerated to form acceptable particles. However, in all of the above work it was found that when the mass of syrup was stirred in the shaping bath a portion of this solvent mixture was beaten into the cellulose causing the particles to contain bubbles of the solvent and at times to be just cellulose shells. This indicated that the material had to be formed into the proper size particles prior to being added to the shaping solution.

The next experiments were made by dropping viscose, drop by drop, into a mildly agitated shaping solution. First, viscose having a viscosity of 150,000 centipoise was dropped from a spatula. The material was so viscous that the large drops could not be formed into spheres and they were further broken down by the agitation. The smaller particles "rounded up". Next, viscose having a viscosity of 21,000 centipoise was used. Spheres formed with this material under the influence of very mild agitation.

The lowest available viscosity viscose which was available at that time was then used (10,000 cp.). This material had such a great tendency to become spherical that with no agitation at all "strings" of syrup about five to six inches long and 1/8 to 1/4 inch in diameter broke down into perfect spheres.

This experiment suggested the possibility of forming the spheres by dropping viscose drop wise into a "shaping" solution and allowing the droplets to fall through this solution into a higher density hardening (coagulation) bath.

Experiment No. 8

After the preliminary work described above, some of the cellulose spheres were shown to the customer. The product seemed good enough that a cooperative program was established. The feature liked most by the customer was the roundness of the spheres, as those made in the preliminary experiments described above were almost perfectly spherical and certainly better than any of those produced by the customer in his own work. The viscose prepared in the laboratory was, of course, not of the same quality as commercial viscose because of a lack of proper type of equipment. In order to eliminate this variable the customer agreed to provide commercial viscose of the type used by him in his experimental production. The experimental work that follows was done with commercial viscose shipped to t e laboratories in well insulated thermos jugs.

In order to test the idea described above of dropping the viscose through a supernatant shaping liquid and thence into a hardening liquid the following experiments were performed.

Commercial viscose having a viscosity of 12,400 centipoise was allowed to drop from a separatory funnel having an outlet tube of approximately 3/16 inch diameter. The drops were allowed to fall into a 250cc glass cylinder to determine desirable densities for the "shaping" and "hardening" liquids so as to impart a desirable rate of fall to the viscose drops. It was determined that a shaping bath should have a specific gravity of 1.115 and the hardening bath a specific gravity of 1.120 both measured at 20°C.

A glass tube one inch in diameter and four feet long was stoppered at the lower end and supported in a vertical position. The lower six inches were filled with a hardening (salt) solution, and the remaining 42 inches with the shaping solution.

The viscose was then added drop wise from the funnel and it was found that by the time the droplets reached the interface of the two liquids they had formed perfect spheres. The spheres, would not, however, break the interface and enter the hardening solution. The result was that the spheres "hung up" at the interface and coalesced. Some of the drops could be made to pass into the lower liquid by shaking the tube, however it was found that these were deformed by the holdup.

Experiment No. 9

An attempt was made to drop the viscose into coagulating solutions directly. Solutions of sodium sulphate from 1 to 13% were tried as well as ammonium sulphate from ¼ to 1% and aluminum sulphate from 1 to 2%. In all cases, however, the coagulants hardened the surface of the particles before they became spherical and the resultant product was "tear drop" shaped.

Experiment No. 10

In order to overcome the "hanging up" of particles at the interface of the hardening and shaping solutions when the latter was placed over the former in a tube, which seemed to be the chief difficulty of this system, a wetting agent was added to the salt solution.

A shaping bath having a specific gravity of 1.090 at 20°C. was placed above an alum solution having a density of 1.105. The latter solution had 1% by weight of the wetting agent Aerosol MA.

The droplets of viscose became spherical in falling through the shaping bath and passed through the interface without hang up into the coagulant. The particles were round but had a wrinkled surface. It was suspected that this was due to the rate of coagulation produced by the alum so a new bath containing sodium sulphate and 0.05% Aerosol MA was substituted for the alum solution.

Drops from the dropping funnel formed spheres just before reaching the hardening solution. They "hung up" for an instant and then fell through. The shaping solution column was 8" deep and the hardening solution 2½" deep. The particles were leached in 20% sodium sulphate for one and one-half hours at 80° to 90°C. and washed by allowing warm water to circulate into a beaker of the pellets over night. The spheres looked very good, being round, smooth and transparent.

Experiment No. 11

Results of Experiments No. 8, 9 and 10 showed that spherical, regenerated pellets of cellulose could be made by the following process.

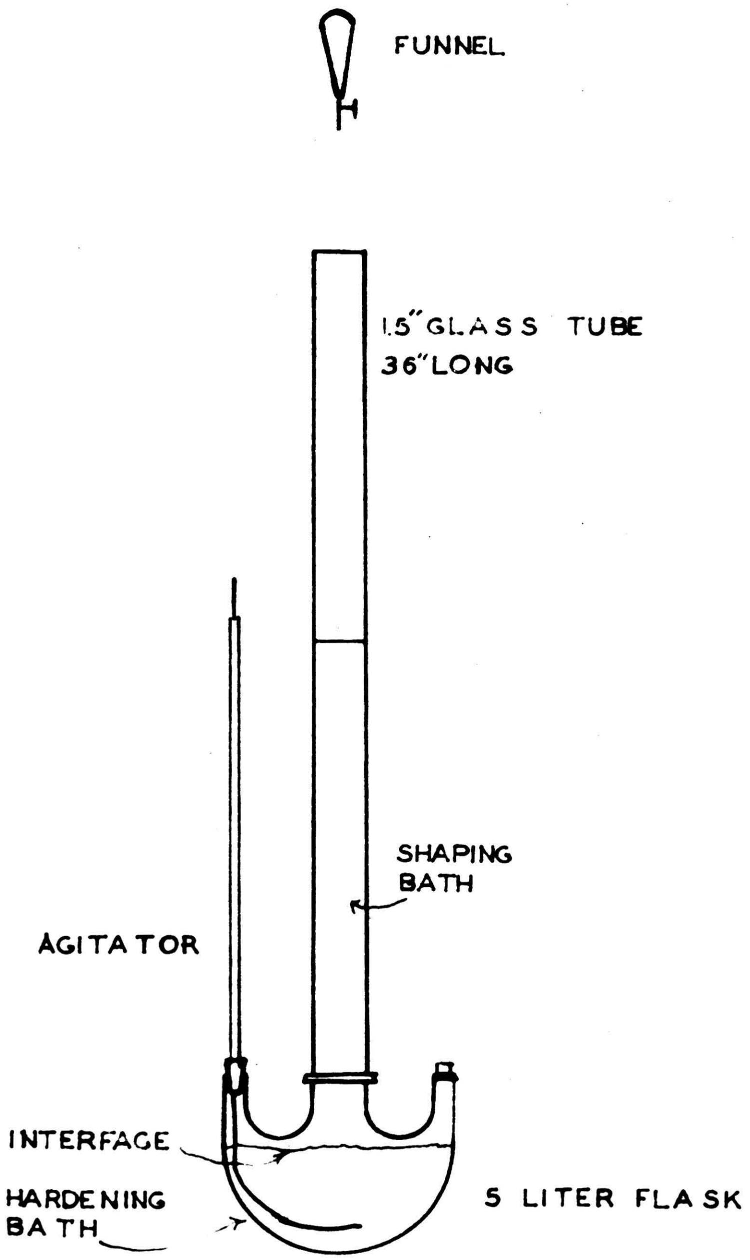
Allow droplets of cellulose zanthate solution to be dropped through an air space into a mixture of benzene and carbontetrachloride of such proportions that the specific gravity of the solution is only slightly less than that of the cellulose solution, and of such a column height that the fall of the drops of viscose syrup through this liquid causes the individual droplets to become spherical. This shaping liquid of the mixed organic solvents is supernatant to a solution of sodium sulphate containing a wetting agent to facilitate the passage of the viscose sphere from the supernatant liquid into the coagulating salt bath. The drops must be suspended in the salt solution by mild agitation until regeneration has proceeded sufficiently to change the syrup into firm, rubbery cellulose.

The above procedure was developed by dropping the viscose into these solutions in a cylinder about 1½" diameter. Naturally the production of pellets in this equipment was limited to just a few particles in each experiment. In order to obtain larger quantities to supply the customer for his approval it was necessary to improve the set-up. The next apparatus was as shown in Figure 1. The main part of this equipment was a 5-liter, three-necked flask and a 1½" diameter tube 36" long which was inserted into the center neck of the flask. One of the small necks was sealed and an agitator was inserted in the other. The agitator designed for this apparatus consisted of a piece of rubber tubing on the end of a piece of glass stirring rod. This type of agitation was used because only a mild agitation was necessary to suspend the globules in the coagulating liquid. Secondly, only the gentlest of agitation could be tolerated because of the tendency for the two liquid phases to mix. This frequently occurred because not only were the specific gravities of the liquids very close, but the lower liquid contained a wetting agent.

The first complete experiment (Experiment No. 11) made in the apparatus described above was made by putting a sodium sulphate solution having 0.05% Aerosol OS and a specific gravity of 1.120 in the five liter flask so that the liquid level was well below the neck of the flask. A mixture of C_6H_6 and CCl_4 having a specific gravity of 1.105 was carefully floated on the salt solution. Enough of this mixture was used so that the liquid extended to a height of

LABORATORY EQUIPMENT

FIG. 1



15 to 16 inches in the tube. The transferring of the viscose to the separatory funnel which was used to form the drops caused a quantity of air to be entrapped in the viscous syrup. In order to minimize the effect of the air an aspirator was attached to the funnel to remove the large bubbles. Everything worked well except the pellets settled in the bottom of the flask and flattened and coalesced, no attempt having been made to agitate the system in the first experiment.

In the second experiment (Experiment No. 12) the above procedure was repeated except that an attempt was made to prevent the coalescence of the pellets at the bottom of the flask by adding a protective colloid (Swift and Company's Protective Colloid No. 1). The high concentration of the salt caused the colloid to precipitate and this experiment was consequently unsuccessful.

Experiment No. 13 was the first successful experiment made on this scale. An agitator of the type described above was inserted in the flask.

A coagulating solution containing 0.06% Aerosol and sufficient sodium sulphate to cause the density to be 1.120 was used, 833 ml of this solution was placed in the flask. A shaping solution having a specific gravity of 1.105 was carefully added so as to prevent a mixing of the phases. The viscose was allowed to drop from the funnel one drop at a time. Throughout the entire time required for the addition of the syrup the system was gently agitated with the rubber tube at the end of the glass rod. The agitation was vigorous enough to prevent the particles from settling at the bottom of the flask but nonetheless gentle enough to prevent a mixing of the phases. At the end of the addition, the particles were removed and placed in a saturated sodium sulphate solution and heated for one hour at 90°C. The purpose of this treatment was to complete the regeneration of the zanthate. The pellets were then washed in running, warm water over night. The pellets were spherical, smooth and clear.

The above experiment was repeated successfully in Experiments No. 14, 15 and 16. The only change in the experiment being that the salt solution in the last two experiments had a specific gravity of 1.115. The data pertinent to the above batches are summarized in Table No. 1.

Pellets made in Experiments No. 13, 14, 15, and 16 were sent to the customer for his examination. His report follows:

"<u>Quality of Your Sample</u>

1. We received 41 pellets which were the result of "test tube size" experimental batches.

Table No. 1

Summary of Results with Five Liter Equipment

Experiment	Specific Gravity of Na_2SO_4	Aerosol OS%	Specific Gravity of Shaping Solution	Remarks
11	1.120	0.05	1.105	Pellets rounded up. Passed through interface freely. Pellets settled and adhered to one another.
12	1.120	0.05	1.105	Protective colloid added to salt solution to prevent coagulation of the pellets. Colloid precipitated. Experiment unsuccessful.
13	1.120	0.06	1.105	Grains shaped, fell through interface freely. Particles suspended in coagulating bath with mild agitation. Product acceptable.
14	1.120	0.056	1.105	Duplicate of batch 13. Test was successful.
15	1.115	0.057	1.105	Same procedure as previous day. Test successful.
16	1.115	0.056	1.105	Repeat of previous experiment. Test successful.

2. In color, density, and roundness they compare excellently with our product. The average diameter of 82 mils is about 10% under our desired 90 mils and the ratio of average Major and Minor diameter of 1.05 as compared with our desire of 1.25 or better is very good. We are very pleased with this progress. The majority of your sample comprised light amber translucent pellets with a few, about 10%, slightly darker.

Further test details include:

Average Major diameter	84 mils
Average Minor diameter	82 mils
Range of diameters	
Major (all)	77-101 mils
Major (omitting 1 large pellet)	77-89 mils
Minor (all)	71-96 mils
Minor (omitting 1 large pellet)	71-82 mils
Approximate Specific Gravity	1.57
Number of Balls per Pound	60,000

The large pellet referred to above had major, minor, and average diameter of 101, 96, and 98.5 mils and a diameter ratio of 1.05. This indicates that pellets of our dimensional interest can be made by your process."

No further work was done with this equipment because of its limited capacity. The customer required at least one pound of pellets for an adequate evaluation and, therefore, work in the laboratory set-up was stopped and plans made for larger scale experiments. This is reported in Section V. Production of One Pound of Pellets.

V. Production of One Pound of Pellets

The results of the preliminary experimental work described above, culminating in the development of the dropping apparatus shown in Figure 1 encouraged us to enter the next phase which was the preparation of a one pound sample of pellets for the customer.

Apparatus designed and assembled for this operation is shown in Figure 2. The essential parts were as follows:

Viscose Dropper

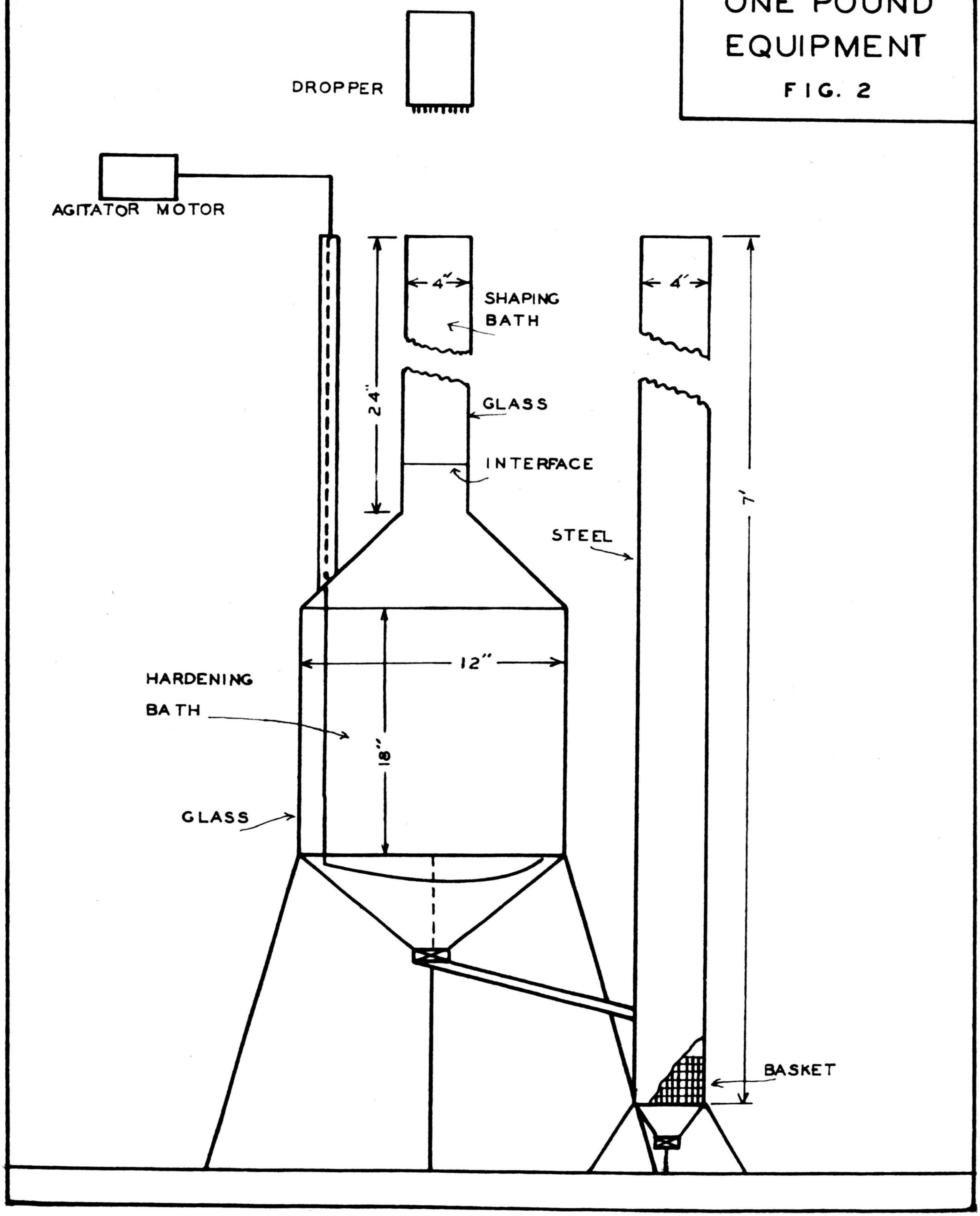
The viscose dropper, the design of which was one of the only features that was varied throughout the seven experiments made with this apparatus, consisted of multiple dropping tubes from a "constant head" feed tank.

Shaping Tube

A piece of four inch diameter glass pipe 24 inches long was used to contain the shaping bath. In most of the experiments the interface between the two liquids was located in this tube. A glass tube was used so that the particle shape could be examined throughout the dropping period, as the effect of the height of the shaping liquid and the height of fall before entering the liquid has an effect on the shape of the particles. Optimum column height varies with the age and viscosity of the viscose.

ONE POUND EQUIPMENT

FIG. 2



It was also necessary to observe the passage of the drop through the interface and also the condition of the interface, which if disturbed caused emulsification of the two phases.

Coagulating Bath

The coagulation bath was made from a glass sight glass having a diameter of twelve inches and a length of eighteen inches. It was considered that this portion had to be of glass because of the necessity of visually controlling the agitation, and the condition of the interface should it have been necessary to position the interface in this portion of the apparatus. The agitator consisted of a rubber diaphram eight inches by five inches fixed at one end, and fastened to a reciprocating rod at the other. The rod was attached to a cam with a one-eighth inch offset. The height of stroke was adjustable, and was usually set at 1/2 inch stroke. The speed was maintained at 49 strokes per minute.

Pellet Withdrawal

In order to make it possible to withdraw pellets without stopping the dropping of syrup and to prevent any disturbance to the interface, a constant level device consisting of a four inch diameter black iron pipe was connected to the bottom of the coagulating section. Periodically the valve at the bottom of the agitated hardening section was opened and the pellets passed down the draw-off pipe into the constant head pipe in the bottom of which was placed a wire basket. The basket was withdrawn from the pipe manually when it was filled with pellets.

Regenerating Bath

The partly regenerated pellets removed periodically from the column were placed in glass beakers and placed on laboratory hot plates. The pellets were agitated with a laboratory stirrer.

Drying

For the most part the pellets were air dried; however, final drying was accomplished in a laboratory oven.

Results of Experiments in "One Pound" Equipment

A total of seven separate lots of pellets were made with this equipment, the first on July 28, 1944, and the last on September 16, 1944.

Preliminary Work - Selection of Dropping Tips

The customer require pellets having a diameter of 90 mils. In order to obtain a particle of that size, after it had been regenerated, it is necessary to form a much larger globule of the syrup since it contains only approximately 6.25% cellulose. Therefore, the weight of the viscose globule was calculated as follows:

Per Cent Cellulose in syrup	6.25%
Specific Gravity of syrup	1.12
Per Cent Cellulose in final pellet	.97%
Diameter of final pellet	0.090 inches

$$\text{Wt. of Pellet} = \frac{(1)\ (3.14)(.090)^3(1.6)(62.4)}{(6)\ (1728)} = 22.08\text{x}10^{-7}\ \text{lbs.}$$

$$\text{Wt. of Viscose} = \frac{22.08 \times 10^{-7}}{(0.0625)(0.97)}(454) = 0.1658\ \text{grams}$$

Diameter of viscose globule

$$\frac{22.08\text{x}10^{-7}(1728)}{(.0625)(1.12)(62.4)} = 0.008735\ \text{cubic inches}$$

$$\frac{(6)(0.008735)}{3.14} = 0.2558\ \text{inches}$$

Having determined the weight of the drop of syrup required to produce the 0.090 inch dry, regenerated pellet it was necessary to determine empirically the dimensions of glass tubes that would produce a free falling drop of this weight.

Glass tubing having outside diameters of 0.25, 0.26, 0.28, 0.30 and 0.32 inches were obtained to determine the most suitable size for the dropping tube. This approach was justified because the drops produced by the separatory funnel used in the previous experiments had produced pellets having a diameter of 0.082 inches. It was reasoned, therefore, that the simplest way in which to obtain the proper tube size would be empirically rather than through calculation based on theory of drop formation. Syrup was allowed to form from tips made of each of the above sizes and the size of the resulting drops were compared visually with the drops produced by the funnel. Only the 0.30 and 0.32 tubes seemed to produce pellets apparently having the desired size.

Next these tubes were tested to determine the actual weight of viscose of free falling drops from these tubes. The data are summarized in the following table.

Table No. 2

Weight of Viscose Produced
by
Selected Glass Tubes

Trial No.	Diameter of tip in inches	Weight of 30 drops in grams	Weight of one drop in grams
1	0.30	3.095	0.103
2	"	3.278	0.109
3	"	3.047	0.102
1	0.32	4.577	0.152
2	"	4.824	0.161

Since the tube having an outside diameter of 0.32" produced viscose globules approaching that which was needed, it was decided to use that tube in the first test.

Experiment No. 1

The apparatus shown in Figure 2 was used except that the dropping head consisted of four separatory funnels each equipped with the special 0.32 inch od. tube which was connected to the funnel with a short piece of rubber tubing. The agitator was a small metal flap.

The method of dropping was not satisfactory and it was observed that the changing head in the separatory funnels affected the drop size.

Air was incorporated in the syrup when it was placed in the funnel and this is undesirable.

The agitator as designed was not good enough and the pellets settled at the bottom and coalesced.

Experiment No. 2

The apparatus used in the first experiment was modified by adding the flap of rubber as described on page 27. A glass tube was fitted with a rubber stopper and fitted with seven glass capillary tubes each having an outside diameter of 0.375 inches. Another larger diameter glass tube was placed around the dropping tube so as to serve as a cooling jacket for the viscose tube. This was considered necessary in order to maintain constant viscosity for the drops and also to prevent accelerated ripening of the viscose.

This experiment was successful and about 200 grams of finished product was obtained.

It was observed during the course of the experiment that the method of pouring syrup from the thermos jugs into beakers and thence into the dropping funnel caused a considerable quantity of air to be entrapped in the syrup and some of the air ended up in the globules.

Experiment No. 3

Experiment No. 3 was to be run in the manner of batch No. 2; however, the available viscose had ripened to the point that it would not flow from the dropping tubes.

Experiment No. 4

This experiment was unsuccessful because the shaping bath which was made to have a specific gravity of 1.106 actually had a specific gravity of 1.095 after it had been placed in the equipment. The pellets would not become spherical in this low density solution even though the height of the solution was increased from a normal 18 inches to 36 inches.

Experiment No. 5

The apparatus was prepared as in previous batches. The viscose height was maintained at 8 inches because this amount of viscose produced 25 to 30 pellets per minute which was considered a satisfactory rate and because there was a minimum of secondary drops formed with this head. The shaping bath was kept at 19 inches and the dropping tube was placed 13½ inches above the liquid level; these positions seemed to produce the best spheres.

Pellets were removed from the bottom of the hardening bath approximately every two hours. A total of 23 separate lots of pellets were collected from this batch during the duration of the run.

Experiment No. 6

The data collected for this experiment follows:

1. Specific gravity of viscose 1.121. Viscosity 5,680 centipoise.

2. Time started: 1:30 p.m. Shaping bath unsatisfactory and replaced. Run resumed 4:30 p.m.

3. Outside diameter of dropping tip 0.368 inches.

4. Inside diameter of dropping tip 0.112 inches.

5. Number of tips used - 7.

6. Height of tips above liquid - 9½ inches.

7. Viscose Head - 6 inches.

8. Temperature of viscose - 13° - 23°C.

9. Average weight of viscose drop - 0.12 grams.

10. Rate of drop formation - 50 drops/minute.

Data on Shaping Bath

1. Liters of solution in shaping bath - 4 liters

    Volume of carbontetrachloride - 1.25 "

    Volume of benzene - 2.75 "

2. Specific gravity of bath - 1.106

3. Height of shaping bath - 18 inches.

4. Temperature of bath - 25°C. at 1 P.M.
   27°C. at 8 P.M.

5. Rate of fall of drop - 18 inches per 13 seconds.

6. Shape of pellets - 50% flat.

Interface

1. Appearance good at start, by 8 P.M. badly mixed.

2. Cause of change. Shaping bath forming in drops on viscose globule and entering salt solution.

Hardening Bath

1. Liters of sodium sulphate 56

    Grams of salt 7840
    % Aerosol OS 0.051

2. Specific Gravity 1.117

3. Temperature of bath 25°C. at 1 P.M.
    27°C. at 4 P.M.

4. Color of bath - reddish.

5. Physical state of precipitate in bath medium, flocculent.

6. Time pellets taken from bath: 7:30 P.M.
    8:00 A.M.

7. Weight of pellets 339 grams
    800 grams

8. Average size of pellets as taken from the solution 0.160"

9. Color of pellets from bath - gray.

Dehydration Bath

1. Liters of concentrated sodium sulphate - 1.5

2. Specific gravity of solution at start - 1.186
    Specific gravity of bath after 2 hrs. - 1.186
3. Temperature of bath - 80°C.

4. Time to complete regeneration - 2 hours.

5. Color of bath at beginning - clear.

6. Color at the end of two hours - blue gray.

7. Weight of pellets removed - 164 grams
    444 grams

8. Color of pellets - gray

VI. Pilot Plant

The success of the experimental work on the small scale encouraged us to build and test a pilot plant for the production of a minimum of twenty pounds which were required by the customer in order to adequately test the product made by the new process.

Two, ten-pound lots of regenerated cellulose pellets were produced from viscose syrup. The first ten-pound lot was regenerated from commercial viscose syrup. This syrup had a specific gravity of 1.123 at 20°C. The viscosity, at an age of six to seven ml. of 10% ammonium chloride solution was 5000 to 7000 centipoise. (All age tests were made by the Hottonroth ammonium chloride method(5) which, briefly, is the volume of 10% ammonium chloride solution necessary to coagulate a small quantity of viscose. This is an indication of the degree of ripening that has occurred.

The second ten-pound sample was regenerated from three batches of Western Cartridge viscose. The three batches had specific gravities of 1.109, 1.115, and 1.123 @ 20°C., viscosities of 6195, 11390, and 5960 centipoise respectively. The respective ages corresponding to the above viscosities

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(5) Ott, Emil, Editor Cellulose and Cellulose Derivatives, 1943
Interscience Publishers, Inc. New York, N.Y.
P. 837

were 7.1, 6.9, and 9.2 ml. of ten percent ammonium chloride solution. Each 10-pound lot was divided into three different groups as follows:

2 pounds of pellets having diameters of 0.060 ± 0.005"
2 pounds of pellets having diameters of 0.075 ± 0.005"
6 pounds of pellets having diameters of 0.090 ± 0.005"

Apparatus Used:

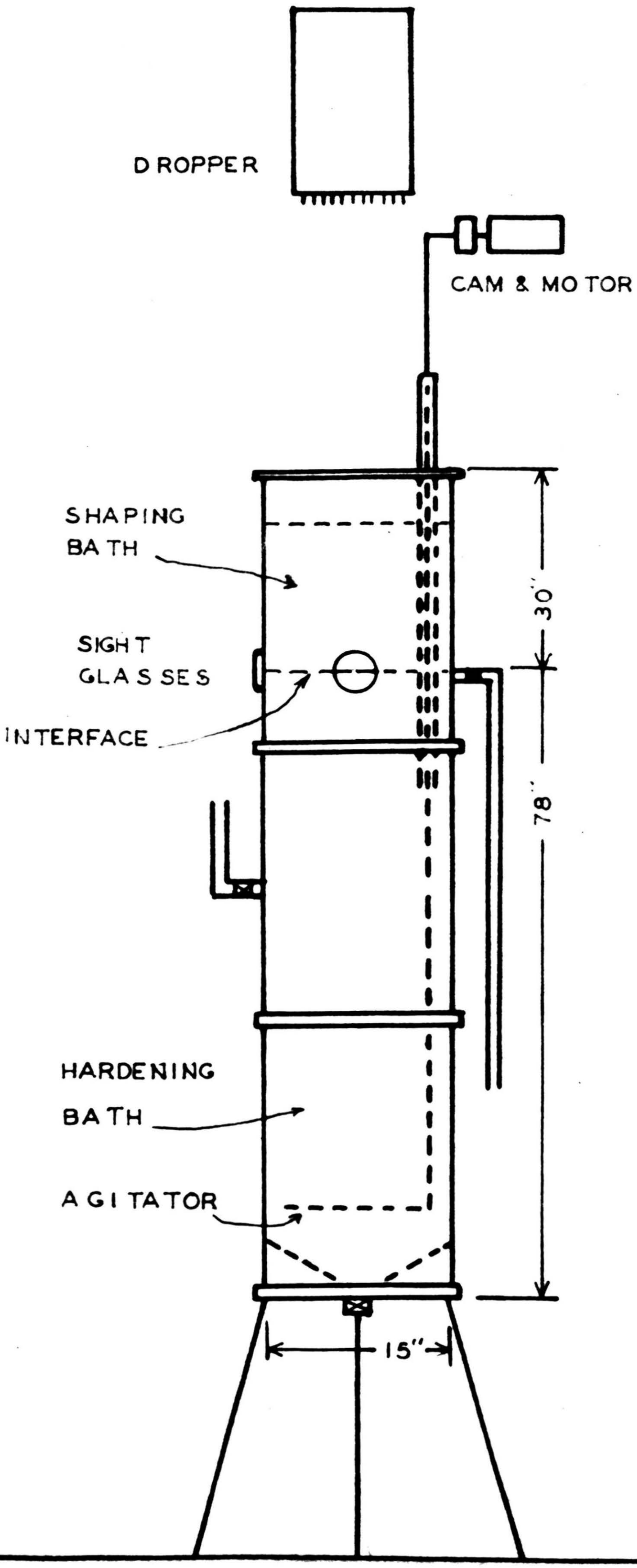
The apparatus consisted of a dropping plate, a pellet-forming column solution, a dewatering and leaching tank, a dryer, a de-tailer, and a screen.

The dropping plate was made from a 6 gallon can 14 1/4" high, 12" in diameter at the top, and 11 1/2" in diameter at the bottom. The bottom was cut from the can and replaced by two 1/16" steel plates separated by a 1/4" disc of Korseal. The diameters of the plates were 13". A circle having a diameter of 11" was inscribed in the center of the plates. This circle was marked by 2 perpendicular diameters 1" wide. The quarters of the circle thus formed were each perforated with fifty 7/16" holes having a distance of 5/16" from center to center. The Korseal sheet was perforated with holes just large enough to hold dropping tubes firmly. The glass dropping tubes were 3/4" in length. The inside and outside diameters of the dropping tubes for the various size groups of pellets were -

Size of Pellets	Bore of Tube	Outside Diameter of Tube	Outside Diameter of Tip
0.060"	0.090"	0.153"	0.090"
0.075"	0.118"	0.192"	0.118"
0.090"	0.118"	0.356"	0.356"

PILOT PLANT EQUIPMENT

FIG. 3



The assembled plate was fitted on the top surface with a Korseal gasket 1/16" thick. The plate was held firmly against the bottom of the bucket by means of 1/8" brass rods extending through the plate along the outside of the bucket and hooking on the top of the bucket. Adjustments were made by means of nuts on the bottom side of the plate. Four of the rods spaced at 90° angles were hooked onto a cross of steel rods lying on top of the bucket and extending 3" on each side. These rods, clamped to vertical rods extending from the sides of the column, held the dropping bucket above the column.

The pellet-forming column was made of three flanged, black steel tubes three feet long with an inside diameter of 15 inches. The sections were bolted together to form a cylinder nine feet high. The cylinder had a conical bottom with a two inch opening through which the product was withdrawn. Eight inches from the bottom of the cylinder a circular, stainless steel, eleven-inch diameter plate, hinged to the column on one side and to an agitator rod on the other side, served to give an up and down agitation in the lower six feet of the column. The power for agitation was supplied by a motor, speed reducer and cam arrangement located at the top and to the side of the column. In order to prevent a disruption of the interface the rod was enclosed in a guide pipe. The guide pipe, which was four feet long, was fastened at the top of the column.

Four 1/2" steel rods 36" in length, welded on the inside and at the top of the column at 90° intervals, served as supports for the dropping plate.

Two, six-inch sight glasses placed at a 90° angle were fastened into the column 30 inches from the top. This upper 30 inch section contained the shaping bath of carbon-tetrachloride and benzene. The lower 6 1/2 foot section contained the hardening bath of sodium sulfate solution. A 1 1/2 inch hole 30 inches from the bottom of the column provided for the addition of fresh salt solution to replace that withdrawn through the plug-valve with the pellets.

The dewatering tank consisted of a five gallon agitated vessel filled with 16% sodium sulfate solution at 90°C.

The leaching equipment consisted of a forty gallon tank equipped with air agitation and steam coils. Boiler condensate for washing was introduced at the bottom and withdrawn at the top.

Drying of pellets was done in a Pilot Plant Proctor-Schwartz dryer.

Screens with openings of 0.095", 0.085", 0.080", 0.070", 0.065" and 0.055" were used for sizing the samples.

Raw Materials Used:

The raw materials used were commercial carbontetrachloride, benzol, sodium sulfate, viscose, Western Cartridge viscose, and boiler condensate water, Aerosol OS, carbon disulphide, and sodium hydroxide.

Procedure:

Viscose as received was stored at a temperature of 4 to 5°C to prevent premature ripening, and when needed, was ripened at an accelerated rate at a temperature of 15 to 20°C. The viscose, having a viscosity of 7000 to 9000 centipoise and an age of 6 to 7 ml. of 10% ammonium chloride solution, was introduced onto the dropping plate from a 2 1/2 gallon pickle jar fitted with a lid containing a one inch glass delivery tube, barely extending through the lid, and a small glass tube air vent extending to the bottom of the jar. The one inch tube was 16 inches in length and the height of the bottle was so adjusted that the exit end of the tube was about one inch from the bottom of the bucket, thus avoiding the incorporation of air bubbles in the viscose. The viscose head above the plate was kept at 5 inches.

The viscose drops formed by 120 dropping tubes fell through a 15 inch air column into a shaping bath of carbontetrachloride and benzene having a specific gravity of 0.016 less than that of the viscose @ 20°C. The height of the shaping bath column varied from 10 to 18 inches depending on the viscosity of the viscose. This adjustment was necessary in order to form the drops into spheres.

The spherical viscose drops from the shaping bath passed into the regenerating bath. This solution had a specific gravity 0.006 less than that of the viscose @ 20°C.

The spheres were kept suspended in the solution by agitation until they were sufficiently hard to permit removal without destroying their sphericity. (The time was one hour in most cases.)

The partially regenerated pellets were placed in the dewatering bath containing 16% sodium sulfate where regeneration was completed. The pellets were agitated in this solution for two hours at 90°C.

The regenerated pellets were placed in the leaching bath and leached in a stream of boiler condensate water @ 90°C. The treatment was continued until a sample of the pellets, dried at 100°C for 2 hours, showed no discoloration. The time required for leaching five pounds of pellets in most cases was 24 hours and the rate of flow of condensate water was 20 gallons per hour.

The leached pellets were placed in a Proctor-Schwartz drier and dried at 60°C for the first 8 hours, then further dried at 75°C for 2 hours.

The dried pellets were de-tailed (misshapen pellets removed) and screened to obtain the three groups having average diameters of 0.090", 0.075", and 0.060".

Preparation of Viscose:

Apparatus Used

The apparatus consisted of a hammer mill, press, shredder, xanthation churn, mixing tank, and storage tanks.

1. The Pilot Plant Dixie Mill equipped with a 3/4 inch screen was used for grinding the cellulose sheet.

2. The press consisted of a Charles Elms Engineering Company press frame. This frame was equipped with a 20 ton Blackstone hydraulic jack and a stainless steel cylinder.

The cylinder was made from a stainless steel pipe having the following dimensions:

Thickness	5/16 inches
Height	11 inches
Diameter	8 inches

It was perforated with holes 1/4 inch in diameter. The holes were separated from each other by a space of 3/4 inches.

The inside of the cylinder was lined with 100 mesh and 16 mesh stainless steel screens. The 100 mesh screen was placed next to the cylinder wall. The top and bottom of the cylindrical frame work thus formed was fitted with stainless steel plates 7-3/4 inches in diameter and 1/4 inch thick. The top plate was forced down by a 4 inch cubical block of wood. The top side of the block rested against the bottom of the jack, the top part of which was in contact with the upper head of the press frame.

The lower plate of the press frame was fitted with a stainless steel funnel for the draining of excess liquid pressed from the cylinder.

3. The shredder consisted of a slow speed stainless steel agitator and a three gallon bucket. The soda cellulose

press cake contained by the bucket was held lightly against the agitator until the material was thoroughly fluffed.

4. The ten-pound experimental digester was used as a xanthating churn. This digester was equipped with sampling, vacuum and heat control attachments.

5. The mixing tank was a thirty gallon stainless steel tank equipped with a slow speed agitator and a 1-1/2 inch globe valve at the bottom for draining purposes.

6. Two 55-gallon stainless steel tanks and one rubber-lined steel barrel were used as storage tanks. They were fitted with attachments for removal of excess air and carbon disulfide by exhaustion.

Rayonier's Purayonier woodpulp (94% alpha cellulose) was twice ground through the small laboratory phosphor-bronze Dixie Mill before starting other operations.

Two pounds of ground pulp were steeped in 18% sodium hydroxide solution for 30 minutes.

The soda cellulose was then transferred to a press in which it was pressed until a ratio of two parts caustic to one part cellulose resulted.

The ratio was determined (1) by weighing the recovered caustic solution very accurately to ± 1/8 of a pound and (2) by weighing the cake of alkali cellulose crumbs to ± 0.02 pound.

The pressed cake was broken up and fluffed as uniformly as possible by (1) beating with the propeller of a Lightnin' mixer in a ten quart pail, and (2) fluffing and tearing by hand.

The alkali cellulose crumbs were aged in fibre-pak containers at a temperature of 20° ± 1°C for 72 hours.

Xanthation was carried out in the stainless steel digester. The temperature was controlled at 20° ± 1°C for 2 1/2 hours. Three pounds of carbon disulphide were used for xanthation for each eight pounds of alkali cellulose crumbs. Rotation of the digester was started after the addition of 1.4 pounds of carbon disulphide. After twenty minutes, the rotation was stopped and another 1.4 pounds of carbon disulphide was added. Finally, after a total of 130 minutes, the remaining 0.2 pound of carbon disulphide was added and rotation continued for another twenty minutes.

Before removing the cellulose xanthate from the digester, the excess carbon disulphide was removed by (1) applying a 15 inch vacuum to the closed digester for twenty minutes, and (2) passing a small stream of air over the cellulose xanthate for ten minutes.

The cellulose xanthate was dissolved in 5.1% NaOH (Sp. Gr. 1.056) in a stainless steel drum by a slow speed mixer in the following manner:

1st batch in 65 lbs. of 5.1% NaOH
2nd & 3rd batches in 130 lbs. of 5.1% NaOH
4th & 5th batches in 130 lbs. of 5.1% NaOH

The viscose was filtered by straining through a filter barrel containing a 240 x 10 meshes per inch stainless steel screen of Dutch weave.

The viscose was aged under vacuum on a varying schedule as to time and temperature. The purpose of changing temperature was to bring the viscose to a condition at the right time suitable for dropping pellets.

Before reaching an ammonium chloride number of 7.0 the different batches of viscose were drawn off into 2 1/2 gallon pickle jars as used in the pellet dropping procedure. Each of these jars was subjected to vacuum to remove any entrapped air bubbles from the viscose.

Ten pounds of pellets produced from commercial viscose were made as described above and shipped to the customer. Work was immediately started on the production of ten pounds of pellets from viscose which had been made at Western Cartridge Company, since it was felt that the quality of the pellets would depend upon the source of the cellulose zanthate. It was considered necessary to manufacture zanthate at the pellet plant because it ripens at such a rate that it was considered impractical to try to transport it from an outside source.

Each of the ten-pound samples consisted of three lots as follows; two pounds pellets 0.060 inch average diameter;

two pounds pellets 0.075 inch average diameter; six pounds pellets 0.090 inch average diameter.

A tabulation of the properties of the shipment of pellets made from viscose produced in our laboratories follows:

Table No. 3

Summary of Ten Pound Shipment

Physical Characteristics	(1) (.075")	(2) (.060")	(3) (.090")	Specifications
1. M&V* - 40 hours @ 100°C	7.53	5.45	5.45	5 to 8%
2. Sp. Gr. @ 23°C	1.50	1.52	1.51	1.5 to 1.6
3. Weight per pellet in grams	.0049	.0040	.0092	Not specified
4. Pellets per pound	92,653	114,959	51,800	Not specified
5. Bulk density	.902	.918	.901	.93
6. Ash Content in %	.16	.12	.11	.20 or less
7. Weights of pellets shipped in pounds	2.2	2.6	6.35	
8. Average Max. axis in inches	.071	.066	.089	Variation of ≤ .005"
9. Average Min. Axis in inches	.0698	.065	.087	Variation of ≤ .005"
10. Ratio of Max. to Min. Axis	1.02	1.03	1.03	1.20 or less
11. Color	Medium amber, translucent, and clear		Mixed light and medium amber, translucent, clear	
12. Surface	Reasonably smooth and free of wrinkles. The three samples were clean and free of foreign material.			

* M&V - Moisture and Volatile

Data on the yield of pellets is found in Table No. . Since the nature of the experiments in the production of these pellets was intermittent it is reasonable to believe that in a production operation the yield would undoubtedly be high, certainly over 90%.

Table No. 4

Typical Batches Prepared for Yield Data on Second Ten Pound Shipment

Pellet Size	.060"	.075"	.090"
Batch number	1	1	2
Weight of Viscose Dropped	16.5 pounds	48.45 pounds	76.15 pounds
Percent Cellulose	6.16	6.16	6.01
Weight of Cellulose	1.018	3.004	4.58
Weight of Bone-Dried Cellulose Pellets	0.91	2.29	3.34
Weight of Acceptable Pellets (oven dry)	0.85	2.19	3.15
Percent of Acceptable Pellets from Cellulose in Viscose	83.6%	72.8%	68.7%

In the preparation of the above pellets a total of four separate experimental batches were made to produce the 0.090 inch pellets, two batches were made for the production of the 0.060 inch pellets and one batch was made for the production of the 0.075 inch pellets. A complete tabulation of data gathered in the preparation of the batches is listed in the appendix.

Complete physical analysis of the various lots as shown in Table No. 3 were submitted to the customer. Subsequent correspondence with him revealed that a careful examination of the product by him confirmed our analysis. Subsequent chemical and product tests in the end device revealed that the product developed to fulfill the need was satisfactory and negotiations were started for the construction of a plant to manufacture the product.

VII. Proposed 1000 Pound Per Week Plant

The successful conclusion of the pilot plant development and acceptance of the product by the customer led to the design of a commercial plant having a capacity of 1000 pounds per week. The design is shown in Figure No. 4 which is a flow sheet of the process.

In order to determine the requirement for storage capacity and process equipment sizes, a material balance based upon the pilot plant experience was made for the production of 1000 pounds of finished pellets. The complete material balance showing all materials entering and leaving the process at the various stages is shown in Table No. 5.

TABLE NO. 5

Material Balance (Basis: One Week Operation)

Viscose Storage

Entering		Leaving	
Syrup	16,100#	Syrup	16,100#

Viscose Dropper

Syrup	16,100#		16,100#

Shaping and Hardening Column

Shaping liquor			
CCl_4	384#	CCl_4	384#
C_6H_6	460#	C_6H_6	460#
Total	844#		844#

Hardening liquor

H_2O	5,950#	H_2O	5,950#
Na_2SO_4	595#	Na_2SO_4	595#
Aerosol OS	2.4#	Aerosol OS	2.4#
As viscose			
Cellulose	1,045#		
NaOH	1,045#		
CS_2	322#		
H_2O	13,650#		
Sub Total	22,609.4#		6,547.4#
		As pellets	
		Cellulose	1,045#
		NaOH	291#
		CS_2	91#
		H_2O	3,823#
		As liquor	
		H_2O	9,827#
		CS_2	231#
		NaOH	754#
Grand Total	22,609.4#		22,609.4#

Entering		Leaving	
Acidifier			
As liquor			
H_2O	9,827#	H_2O	10,393#
NaOH	754#	Na_2SO_4	1,320#
CS_2	231#	CS_2	231#
		Aerosol	4.5#
As acid			
H_2SO_4 (60°)	912#		
H_2O	270#		
Solution			
Aerosol OS	4.5#		
H_2O	50.0#		
Total	11,948.5#		11,948.5#

Dewatering Unit

Entering		Leaving	
As pellets		As pellets	
Cellulose	1,045#	Cellulose	1,045#
NaOH	291#	H_2O	414#
CS_2 (Products)	91#	NaOH	31#
H_2O	3,823#	CS_2 (Products)	10#
As liquor		As liquor (to sewer)	
H_2O	10,393#	H_2O	13,802#
Na_2SO_4	1,320#	Na_2SO_4	1,320#
Aerosol	4.5#	Aerosol	4.5#
		NaOH	260#
		CS_2	81#
	16,987.5#		16,987.5#

Leaching

As pellets		As pellets	
Cellulose	1,045#	Cellulose	1,045#
H_2O	414#	H_2O	414#
NaOH	31#		
CS_2	10#	As waste H_2O to sewer	
Entering		Leaving	
Condensate H_2O	25,000#	H_2O	25,000#
		NaOH	31#
		CS_2 (Products)	10#
Total	26,500#		26,500#

Drier

As pellets		As pellets	
Cellulose	1,045#	Cellulose	1,045#
H_2O	414#	H_2O	67#
	1,459#		1,112#
		As vapor (waste)	
		H_2O	347#
Total	1,459#		1,459#

<u>Screening - Detailing</u>

As pellets

Cellulose	1,045#	Scrap pellets	
H_2O	67#	Cellulose	105#
		H_2O	7#
		As pellets (To packing)	
		Cellulose	940#
		H_2O	60#
	1,112#		1,112#

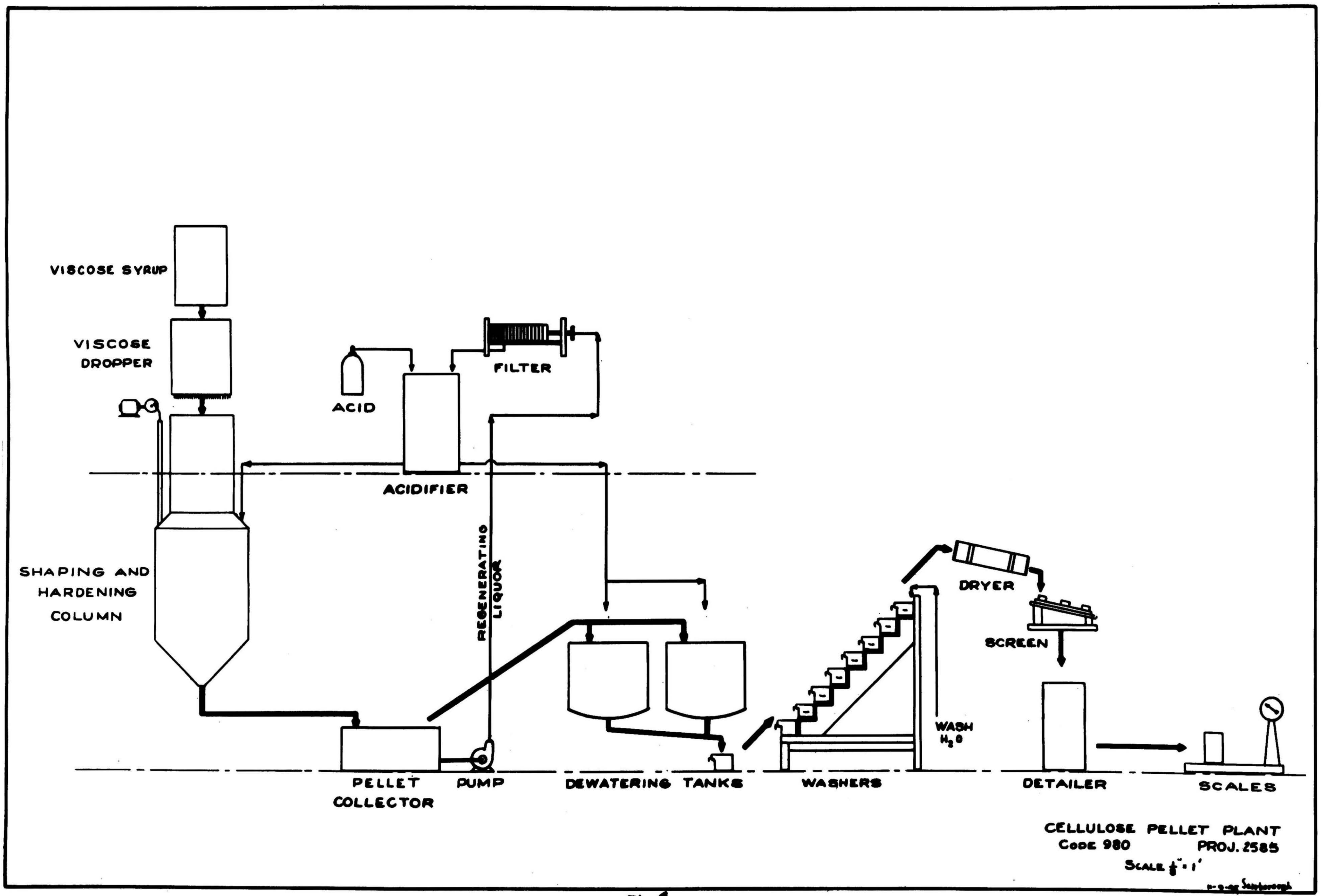

VISCOSE SYRUP
VISCOSE DROPPER
ACID
FILTER
ACIDIFIER
SHAPING AND HARDENING COLUMN
REGENERATING LIQUOR
DRYER
SCREEN
WASH H_2O
PELLET COLLECTOR
PUMP
DEWATERING TANKS
WASHERS
DETAILER
SCALES
CELLULOSE PELLET PLANT
CODE 980
PROJ. 2585
SCALE 1/8" = 1'
Scarborough

Fig. 4

Description of Equipment

With the aid of the material balance, Table No. 5, a detailed list of equipment required to produce pellets at a rate of 1000 pounds per week was prepared. This list described the equipment shown on Figure No. 4 and necessary accessories.

(1) Storage:

1 storage room held at 0°C	715 sq. ft.
1 storage room held at 20-35°C	715 sq. ft.
1 auxiliary storage space	300 sq. ft.

(2) Viscose Dropper:

1 require

Material of construction - mild steel

Size - 35" dia., 30" high

Design: Bottom fitted with 1815 tubes, bore to be specified
Movable vertically over range of 2'
Catch pan to prevent unwanted droplets from entering column
Rack immediately above dropper to hold viscose drum
Stand pipe to regulate flow from drum

(3) Hardening and Shaping Bath:

1 required

Material of construction - mild steel

Size - diameter at top 37"
diameter at bottom 48"
height of top section 36"
height of bottom section 53"
bottom cone, height 29"

Agitation system as follows:

A flapper made from Carlock rubber gasket material firmly hinged at the bottom of the straight side supported by steel ring to be raised and lowered 10-30 times per minute through a distance of 8-12 inches - 1/3 H.P. variable speed motor and cam drive. A secondary agitator affixed to the main agitator to provide agitation in cone. Flapper to be 4" in diameter less than the column.

Auxiliary equipment:

One stand pipe to permit the addition of salt solution below the interface of salt solution and solvent solution. One inch drain line to pellet collector. Plug type valve.

(4) Pellet Collector:

1 required

Material of construction - mild steel

Size - 2' wide, 2.5' long, 3' high, divided at point 6" from one side with a wall 2.4' high so that collecting box has dimensions of 2' x 2' x 2.4' high. The top 0.6' of dividing wall to be equipped with 50 mesh screen to permit salt solution to flow into pump box. Pellet box to be air agitated with 1/4" air line.

Auxiliary equipment:

<u>Pump</u>

15 gal/min. centrifugal, head 52.5'

(5) Filter Press:

1 required, plate and frame - iron
20, one inch frames 12" x 12"
30 psi pressure

(6) Acidifier:

1 required

Material of construction - mild steel

50 gallon capacity

1/3 H.P. 1750 RPM Model - S-1 Lightnin'

(7) Dewatering Tanks:

2 required
Size - 75 gallons
Steam jacketed
Air agitation
Bottom pumping
Material - mild steel

(8) Leaching:

One counter current washer, 8 compartments.
Each compartment to be stainless steel clad metal box 26" long, 18" wide, 15" high, equipped with handles on each side.
Overflow weir to be run length of one side of box.
To be screened with 50 mesh stainless steel wire.
Overflow box and pipes to extend horizontally 3" drain to compartment below to extend to bottom of box.
Each box to be equipped with 1/4" air and 1/4" steam dispersers. Put cork on outside, rubber tube connection to air and steam lines. Compartments to be arranged in stair step fashion.
Steps on each side to permit two operators to advance compartment periodically.
Hot tap or condensate water to be supplied at top of leacher. Discharger water from bottom compartment to sewer.

Ten compartments to be supplied. (8 active compartments, one receiving discharge from dewatering tank, one feeding drier.

(9) Drier:

1 required
Rotary type
10" diameter 36" long
Stainless steel
1/4 H.P. motor
1/20 H.P. blower

(10) Screen:

1 required
Vibrating flat bed
12" x 30" screen bed
1/4 H.P.
Two screen beds ,(top and bottom screens)

(11) Detailer:

1 spiral detailing tube required

(12) Packing:

One 0 - 150# scale required

VIII. CONCLUSIONS

1. Spherical particles of cellulose, regenerated from viscose syrup can be made having a diameter as large as 90 mils, a specific gravity in excess of 1.5 and a ratio of major to minor diameter of less than 1 to 1.05.

2. The particles as described in (1) above can be made with reasonably smooth surface, free of nibs.

3. A suitable process for manufacturing cellulose pellets as described in (1) and (2) above consists of the following steps:

    (a) Preparation of cellulose zanthate by conventional methods

    (b) Forming drops of cellulose zanthate having a desired cellulose content

    (c) Dropping globules through an air space and an immiscible liquid such as carbontetrachloride and benzene combined so as to have a specific gravity slightly less than that of the syrup

    (d) Allowing spherical particles from Step (c) to enter coagulating bath to regenerate the cellulose.

    (e) Maintaining the coagulated viscose pellets in suspension in the coagulating bath until the pellets are completely regenerated.

IX. SUMMARY

This report has described the development of a new process for the manufacture of spherical pellets of cellulose regenerated from viscose. The report includes research results on preliminary unsuccessful experiments, preliminary tests of the new method, and the testing of the process in a pilot plant designed and built for that purpose. Also included are the pertinent design information for a 1000 pound per week plant. This includes a material balance from which equipment size and storage capacities can be determined and a description of equipment suggested for the plant.

United States and foreign patent applications have been filed on this process and the product. Patent No. U.S. 2,543,928 was issued on the process on March 6, 1951.

APPENDIX A

RECAPITULATION OF PILOT PLANT DATA

The data collected during the operation of the Pilot Plant using Olin viscose is shown on Table No. 6.

TABLE NO. 6

RECAPITULATION OF PILOT PLANT DATA

Batch No.	Drop Size	Age of Viscose in Ml. of 10% NH_4Cl	Sp. Gr. @ 20°C.	Viscosity in C.P.	No. of Drops/Min/ Tip	No. of Tips Used	Wt. of Viscose Dropped (Pounds)	% of Cellulose in Viscose	Wt. of Pellets Produced (Pounds)	Wt. of Acceptable Pellets (Pounds)
1	0.090"	7.1	1.109	6195	6	120	39.4	6.16	.95	.72
2	0.090"	6.9	1.115	11390	3	120	109.3	6.01	2.47	2.13
3	0.090"	6.4	1.115	11270	2	120	76.5	6.01	3.6	3.40
4	0.090"	9.2	1.124	5960	6	120	120.2	6.71	5.28	1.76
5	0.075"	7.1	1.124	6195	12	162	48.5	6.16	2.48	2.37
6	0.060"	7.1	1.109	6195	4	120	16.5	6.16	.95	.88
7	0.060"	9.2	1.124	5960	4	120	82.0	6.71	3.19	2.81

Batch No.	% of Acceptable Pellets in Desired Size Range	Ash Content of Pellets %	Moisture and Volatile %	Shaping Bath Height Inches	Sp. Gr. of Shaping Bath at 25°C	Volume of Hardening Bath Gallons	Sp. Gr. of Hardening Bath at 25°C	Regeneration Time Hours	Leaching Time Hours	Weight of Pellets Used in Shipment Grams
1	100	.125	5.66	6.25	1.098	60	1.105	2	48	228
2	100	.060	2.75	7	1.104	60	1.110	2	48	887
3	98.5	.11	7.16	12	1.095	60	1.106	4	24	1449
4	100	.16	5.11	8	1.108	60	1.113	2	24	322
5	78	.16	7.3	12	1.104	60	1.110	2	20	1010
6	85	.182	4.65	12	1.104	60	1.110	2	48	231
7	74.2	.102	5.68	8	1.108	60	1.113	2	24	805

APPENDIX B

DROPPING TIPS

Data gathered on the selection of dropping tips is given in Table No. 7 which appears on the following page.

TABLE NO. 7

SELECTION OF DROPPING TIPS

No. of the tip	Bore tip in inches	Outside Diameter of tip, in inches	Outside Diameter of glass tubing used in making tip, in inches	Wt. of 1 drop in grams	Increase in Wt. of drop per 5 inches in viscose head. (grams)	Viscose head in inches.	Rate of drop formation per min.	Average Diameter of pellet in inches.
1.	.118	.356	.356	.112	———	5"	7	.085-.090
	.118	.356	.356	.126	.015	10	16	
2.	.118	.118	.356	.077	———	5	15	.070-.080
	.118	.118	.356	.084	.006	10	17	
3.	.100	.100	.344	.063	———	5	7	.063-.070
	.100	.100	.344	.067	~~.004~~	10	14	
4.	.118	.118	.192	.056	———	5	22	.070-.080
	.118	.118	.192	.067	.010	10	29	
5.	.100	.100	.164	.047	———	5	14	.06 -.070
	.100	.100	.164	.051	.004	10	19	
6.	.072	.072	.156	.035	———	5	5	.045-.060
	.072	.072	.156	.036	.001	10	8	
7.	.090	.090	.153	.056		5	6	.065-.075

Age of viscose used = 6.4cc. 10% NH_4Cl
Viscosity @ 20° C. = 41 sec. or 4,844
Sp. Gr. @ 20°C. of viscose = 1.120

APPENDIX C

PROCESS PATENT

U.S.Patent No. 2,543,928 which was issued on the process described in this thesis appears in this appendix.

Patented Mar. 6, 1951 **2,543,928**

UNITED STATES PATENT OFFICE

2,543,928

METHOD OF PRODUCING CELLULOSE PELLETS

John J. O'Neill, Jr., Roxana, and Emerald P. Reichardt, Alton, Ill., assignors to Olin Industries, Inc., East Alton, Ill., a corporation of Delaware

No Drawing. Application June 19, 1947, Serial No. 755,726

5 Claims. (Cl. 18—47.2)

This invention relates to cellulose, and more particularly to the method of producing regenerated cellulose pellets in substantially spherical form.

Cellulose pellets have a variety of uses, for example, as a raw material for nitration in the formation of a propellant powder, as a gas evolving material in electrical protective devices, as heat insulation, as dielectric material, and as a mild abrasive. It has been proposed heretofore to form cellulose pellets by treating bleached wood pulp with sodium hydroxide and carbon disulfide to form a paste, extruding the paste through a die to form strings, cutting the strings up into pellets and then regenerating the cellulose in the pellets by treatment with acid or other suitable regenerating agent. Such a method, however, does not lend itself to manufacture of spherical or spheroidal particles. Regenerated cellulose pellets of spherical shape provide the advantages, among other things, of being free-flowing and permitting uniform packing with a much wider utility than pellets of non-spherical shape.

An object of the invention is to provide a novel method for producing pellets of regenerated cellulose. Another object is to provide a novel and efficient method for the formation of spheres of regenerated cellulose. Other objects and advantages will become apparent from the following detail description of the invention.

The foregoing objects are advantageously accomplished in accordance with this invention by forming a solution of cellulose, passing drops of the cellulosic solution through a liquid inert thereto wherein they acquire sphericity and then through a liquid interface into a contiguous coagulating bath immiscible with the inert bath wherein the cellulose in at least the surface of the spheres is precipitated to preserve their globular shape.

In carrying out the process the force of gravity is utilized to effect travel of the drops of cellulose solution through the inert or shaping bath into the coagulating bath by formulating the compositions of the cellulose solution, inert bath, and coagulating bath in such manner that they each have a suitable specific gravity. If it is desired that the drops travel upward through the treating baths then the compositions should be so formulated that the cellulose solution has a lower specific gravity than the coagulating bath and so that the coagulating bath likewise has a lower specific gravity than the inert bath. On the other hand, if it is desired that the drops of cellulose solution travel downward through the

treating baths then the compositions should be so formulated that the cellulose solution has a higher specific gravity than the coagulating bath and so that the coagulating bath has a higher specific gravity than the inert bath. In either event it is, of course, necessary that the inert and the coagulating baths be immiscible with each other so that a plurality of treating layers are formed.

Any of the usual cellulose solution processes may be employed, for example the viscose or cuprammonium processes. The regenerated cellulose resulting from such processes has been variously described as "cellulose" and "cellulose hydrate" and it should be understood that the term "regenerated cellulose" as used herein includes the materials so described.

The shaping bath may be formed of any suitable liquid which is immiscible with and does not otherwise react with the cellulose solution and is thus inert thereto and has the proper specific gravity. For instance, a liquid hydrocarbon of low specific gravity and carbon tetrachloride which has a relatively high specific gravity may be mixed in such proportions as to give an inert or shaping bath of proper specific gravity.

The coagulants may be those usually employed with the particular solution process, and the concentration of coagulant may be so adjusted as to give the coagulating solution the necessary specific gravity. For instance, solutions of ammonium salts, or solutions of sodium sulfate, or solutions of sodium sulfate in dilute sulfuric acid are suitable as coagulants for viscose solutions and caustic soda may be employed for coagulating cuprammonium solution. When viscose solution is utilized, it has been found that neutral aqueous substantially saturated solutions of sodium sulphate, i. e., about 10% to about 19% at temperatures in the range of 20° C. to 100° C., are particularly suited as coagulants in the manufacture of smooth-surfaced cellulose pellets and other relatively thick regenerated cellulose articles having at least one dimension of about 0.040 inch to 0.100 inch. The time required for complete coagulation of the viscose solution in such thick shapes may be somewhat shortened by maintaining the concentration of sodium sulphate and temperature as high as possible in the ranges of 10%–19% and 20°–100° C., respectively, while maintaining uniform coagulation.

Complete coagulation may be effected in just one coagulating bath, or, if desired, coagulation may be carried out in a plurality of stages so that only partial coagulation sufficient to fix the cellulose in globular form may be effected in the first coagulating bath and the spheres may then be removed to one or more coagulating baths to complete the coagulation. After coagulation, the spheres may be subjected to acid or other usual treatment to effect complete regeneration of the cellulose and may be washed, dried, screened, sized, and otherwise handled in a manner customary with the solution process and such particulate material.

It has been found that a small amount of a suitable wetting agent incorporated in the coagulating bath facilitates passage of the globules without deformation through the inert liquid-coagulating solution interface. Since the coagulation proceeds slowly, care must be taken to keep the globules in motion in the coagulating bath until they have become sufficiently hardened to resist deformation. In order to avoid insufficient coagulation the specific gravity of the coagulating solution may be so controlled as to cause the globules to pass only slowly through it, and a deep coagulating bath may be employed, or a mild agitation may be utilized which is positive enough to maintain the spheres in free motion within the bath but which is not sufficiently violent to deform the spheres or deleteriously disturb the interface between the liquid layers.

In order to further explain and clarify this invention, following is a typical embodiment thereof in which the preparation of regenerated cellulose spheres utilizing the viscose process is illustrated in detail. In the following example, the globules of cellulose solution are passed downwardly through the treating bath.

Bleached wood pulp having an alpha cellulose content of 94%, of the type employed in the manufacture of rayon, in sheet form was passed through a hammer mill to defiber the sheet. Two pounds of the resulting ground pulp were steeped in 20 pounds of 18% sodium hydroxide solution for 30 minutes at 20° C. The resulting soda cellulose was then transferred to a press and pressed until a ratio of 2 parts caustic to one part cellulose resulted. The pressed cake was then broken up and fluffed uniformly to provide crumbs of alkali cellulose which were then aged at a temperature of 20±1° C. for 72 hours.

After the aging period, 2.1 pounds of carbon disulphide were continuously mixed with 8 pounds of cellulose in the form of such alkali cellulose crumbs for a period of 20 minutes. One and four tenths pounds more of carbon disulphide were then continuously mixed with the ingredients for a period of 130 minutes. The temperature during the mixing with carbon disulphide was maintained at 20°±1° C.

The excess carbon disulphide was removed from the resulting cellulose xanthate by subjecting the mixture to a vacuum of 10 inches of mercury for 20 minutes and subsequently passing a small stream of air over the cellulose xanthate for 10 minutes.

The cellulose xanthate was then dissolved in 87 pounds of 5.1% sodium hydroxide (sp. gr. 1.056). The resulting viscose solution was then filtered to remove any insoluble matter present and was aged under a vacuum of 3 inches of mercury for 18 hours at 20° C. The viscose solution was then allowed to stand and ripen for 8 days at temperatures from 20–30° C.

The aged cellulose solution had a specific gravity of 1.115 at 20° C., a relative viscosity of 11560 centipoises, an age of 7.8 ml. of 10% ammonium chloride (Hottonroth test), and contained 6.01% cellulose, 5.95% caustic soda, and 1.54% sulphur in combination.

The coagulating bath was composed of an aqueous solution of 12% sodium sulphate and 0.045% of the wetting agent, isopropyl naphthalene sodium sulfonate. The coagulating bath had a specific gravity of 1.110 at 27° C. The shaping bath or upper layer of liquid, inert to or unreactive with the cellulose solution, was composed of 68.5% benzene and 31.5% carbon tetrachloride and had a specific gravity of 1.104 at 25° C. The height of this shaping bath or upper liquid layer was 10 inches and the height of the coagulating bath or bottom layer of liquid was 72 inches.

The treatment of the cellulose solution in the baths was carried out at a temperature of approximately 25° C.

The cellulose pellets were then formed by causing drops of the solution to fall from an orifice 0.118 inch in diameter 18 inches through the air into the shaping bath, which drops assumed a spherical shape while passing through this shaping bath through the action of surface tension. As the drops fell from the shaping bath through the liquid interface into the coagulating bath, chemical reaction occurred between the salt solution and cellulose solution resulting in a precipitation or coagulation of the cellulose in the spheres. The layer of coagulating solution was subjected to mild agitation insufficient to disturb the liquid interface between the coagulating solution and the shaping bath and insufficient to deform the globules, in order to prevent the globules from settling on the bottom of the coagulating bath before they were sufficiently hardened to resist deformation. The coagulating or hardening treatment in the coagulating bath was continued for approximately 2 hours and the hardened globules were then removed and placed in a second aqueous coagulating bath which contained 16% sodium sulphate. The globules were suspended in this bath with continuous agitation for 1 hour at 90° C. In order to insure complete coagulation throughout each pellet they were placed in a third bath 16% sodium sulfate for ½ hour at 90° C. The pellets were then washed for 32 hours in water at a temperature of 70–80° C. in order to reduce the ash content to .125%. The pellets were then dried in hot air drier at a temperature of 50° C. for 8 hours and at a temperature of 75° C. for an additional 2 hours with intermittent stirring of the pellets. The pellets were then classified and screened to remove any irregular shaped pellets.

The resulting regenerated cellulose pellets had an average diameter of 88.1 mils with the ratio of major to minor diameters being 1.034 and less, a specific gravity of 1.50 at 23° C., a bulk density of .890, a number per pound of 50,000, and had a smooth surface, like color, and free-flowing characteristics.

Somewhat larger spheres may be formed employing an orifice of the same diameter for the cellulose solution as that employed in the foregoing example, if the orifice is under the surface of the liquid of the shaping bath so that the drop is formed in the shaping bath, instead of being dropped through the column of air. The size of cellulose sphere can be varied also by changing the concentration of cellulose in the solution and by otherwise introducing larger or smaller globules of cellulose solution into the shaping bath, for instance with orifices of different size. When it is desired that the cellulose solution travel downwardly through the treating bath it is preferred that the shaping and coagulating layers have a specific gravity respectively about 0.016 and about 0.006 less than that of the cellulose solution at operating temperature, although lesser or greater differences are operable. When it is desired that the cellulose solution travel upwardly through the treating bath it is preferred that the coagulating and shaping baths have specific gravities respectively about 0.016 and about 0.006 greater than the cellulose solution at operating temperature, although lesser or greater differences are operable. In order to preserve a proper ratio of specific gravity between the cellulose solution, coagulating solution, and shaping baths, it is desirable to carry out the treatment in a vessel equipped with suitable heating and cooling means to provide a relatively constant temperature in the coagulating and shaping layers during the process.

Solid spherical pellets of regenerated cellulose having a specific gravity of 1.45 to 1.6 and a ratio of major to minor diameters of less than 1.05 are readily formed in accordance with this invention.

Although the use of a viscose solution is described in the foregoing specific example, it is to be understood that cuprammonium cellulose solutions and other cellulose solutions may be employed to secure the advantages of this invention and that various changes may be made in the specific details as set forth therein without departing from the spirit and scope of this invention.

Having now described the invention what is claimed as new and desired to be secured by Letters Patent is:

1. In the manufacture of cellulose pellets, the process which comprises introducing drops of cellulose solution into a coagulating bath through an intermediate layer of liquid inert to said cellulose solution, and maintaining the drops of cellulose solution in said coagulating bath at least until the cellulose in the drops is sufficiently coagulated to retain its shape in subsequent handling.

2. In the manufacture of cellulose pellets, the process which comprises forming a solution of cellulose, causing drops of said solution to move freely through a layer of liquid inert to the cellulose solution into a coagulating bath immiscible with said inert liquid and maintaining the resulting globules of cellulose solution in said coagulating bath until the cellulose in said globules is sufficiently coagulated to retain sphericity in subsequent treating and drying operations.

3. In the manufacture of cellulose pellets, the process which comprises introducing drops of viscose solution into a coagulating salt bath containing a wetting agent through an intermediate layer of benzene-carbon tetrachloride mixture, and agitating the resulting globules of viscose solution in said salt bath until the cellulose in the globules is sufficiently coagulated to retain sphericity in subsequent treating operations.

4. A method for the manufacture of regenerated cellulose pellets which comprises forming a solution of cellulose, passing drops of said solution through a liquid inert to said cellulose solution wherein said drops are converted to globules, passing said globules through a liquid interface into a contiguous coagulating bath immiscible with said inert bath, and maintaining said globules in said coagulating bath until the cellulose in the globules is sufficiently coagulated to retain sphericity in subsequent treating and drying operations.

5. A method for the manufacture of regenerated cellulose pellets which comprises forming a solution of cellulose, forming a treating bath having a layer of liquid inert to said cellulose solution and an aqueous layer immiscible with said inert layer containing coagulants for said cellulose solution, with the specific gravity of said layers being so adjusted that a drop of said cellulose solution in said inert layer will move by gravitational force into said coagulating layer, passing drops of said cellulose solution through said inert layer into said coagulating layer, and maintaining the resulting globules of cellulose solution in said coagulating solution until the cellulose therein is sufficiently coagulated to retain sphericity in subsequent handling.

JOHN J. O'NEILL, Jr.
EMERALD P. REICHARDT.

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VITA

John J. O'Neill, Jr. was born in New York, N.Y. on September 13, 1919, the son of John J. O'Neill and Margaret Patterson. He was educated in public schools in Franklin Square, New York, and attended the School of Mines and Metallurgy of the University of Missouri, graduating in 1940 with the degree of Bachelor of Science in Chemical Engineering.

He married Irene Ray of Rolla, Missouri, in 1940, and has one child, a daughter, Anne Marie.

Upon graduation he worked with Joseph E. Seagrams and Sons and joined the Western Cartridge Company, Division of Olin Industries, Inc. in November, 1940, as a Research Chemical Engineer. He has been engaged in various capacities in explosives studies since that time, presently being Head of the Explosives Department of the Research and Development Division.