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MANUFACTURE OF NITROCELLULOSE

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This invention relates to improvements in the manufacture of nitrocellulose and, more particularly, to maintaining special conditions while the nitrocellulose is in the acid wet state whereby the so-called "grain" in the solutions of the nitrocellulose may be substantially eliminated.

For many years manufacturers of nitrocellulose have been bothered at various periods by their product in commercial solutions being defficient in various degrees in quality with respect to "grain". By "grain" those skilled in this art mean an appearance of grain in the nitrocellulose solutions and films deposited therefrom. This particular condition may be readily observed in more exaggerated cases by inverting a glass bottle containing the nitrocellulose solution. The grain will be evident as the solution runs down the side of the bottle. In very severe instances, settling of the grainy material to the bottom of the bottle occurs and is visible by inverting the bottle and observing the settled material. In relatively mild cases the amount of grain present in the nitrocellulose solution may be observed by drawing out a quantity of the solution on a spatula or knife blade and allowing it to form a fan-shaped drip back into the bottle. By looking through the drip the amount of grain present may be readily observed. In general, the grainy portion has the appearance of material not entirely dissolved, i. e., transparent gel-like particles which are decidedly harmful to the uniformity and smoothness of the solution. The grain in a nitrocellulose solution may be rather accurately described as giving an "applesauce" appearance to the solution.

As consumers became more "quality-conscious", the elimination of this undesirable characteristic of graining in nitrocellulose became a very serious consideration. It is particularly objectionable in nitrocellulose solutions designed for use in connection with finishing leather, especially patent leather. In the case of patent leather, grainy solutions give a mottled surface rather than the perfectly smooth, high gloss finish normally obtained. It is also of particular importance that nitrocellulose which is to be used for the production of photographic film base be free of grain. It should be understood, however, that this graining characteristic is objectionable in practically all uses of nitrocellulose, although more particularly so in the above mentioned uses.

Since the graining characteristic of nitrocellulose appears to be more pronounced during the hot months of the year, the trouble seemed to be connected with high temperatures. However, no consistent elimination of the trouble was known until applicant's entry into the field.

An object of the present invention is to provide an economical and practically feasible process for the manufacture of nitrocellulose which will insure a product having uniform absence of grain in solutions, regardless of atmospheric conditions during the manufacture of the product. A further object of the invention is to provide a process of manufacturing nitrocellulose which will give increased yields. A still further object is to provide a process which will prevent denitration or drop in nitrogen content of the nitrocellulose during manufacture.

Another object of the invention is to provide a process whereby filtration losses of nitrocellulose are greatly reduced. Other objects of the invention will be apparent from the description given hereinafter.

The above objects are accomplished according to the present invention by maintaining the nitrocellulose while in the acid wet state in a dehumidified inert atmosphere, preferably dehumidified air.

In the preparation of nitrocellulose, cellulose in any one of numerous forms is treated with nitrating acids to form nitrocellulose, the acids being then separated from the nitrocellulose by a centrifugal separator and the nitrocellulose being subsequently drowned in water. In order to remove the noxious fumes, such as nitrous oxide, et cetera, which are given off during the centrifuging, a force draft of air is drawn through the separator. Although the normal centrifuging period is only two or three minutes, the volume of air passing through the separator is quite large.

Applicant's invention is based on the discovery that the objectionable graining characteristic of nitrocellulose is caused, not directly by high temperature, but by the nitrocellulose while in the acid wet state coming in contact with moist air. Since saturated air at a high temperature contains much more moisture than saturated air at a lower temperature, it is apparent that graining difficulties should be more pronounced during the summer months than during the cold months of the year. For example, saturated air at 90° F. contains 14.8 grains of water per cubic foot while saturated air at 10° F. contains only 0.8 grain of water per cubic foot. It will thus be seen that, indirectly, temperature would be apt to have some connection with graining difficulties, since air at high temperatures is more likely to

have a greater moisture content than air at low temperatures, but the prior art investigators totally failed to appreciate that temperature was not the direct cause of the trouble, and because of this lack of appreciation, they failed to devise a satisfactory method of overcoming graining.

In the ordinary commercial manufacture of nitrocellulose, the nitrocellulose while in the acid wet state may be exposed to the atmosphere for short periods, both prior and subsequent to the centrifuging operation, and therefore in the preferred process the nitrocellulose during the whole time in which it is in the acid wet state is kept in a dehumidified atmosphere, but since the volume of air drawn through the nitrocellulose during the centrifuging is so high, and consequently, the opportunity for the nitrocellulose to absorb moisture during this step is so much greater in proportion than during the rest of the handling of the nitrocellulose before it is drowned, it is sufficient to merely dehumidify the gas applied to the centrifugal separator.

In order to illustrate the effectiveness of the present invention and to show that grain in nitrocellulose solutions may be produced or prevented at will by controlling the moisture content of the air being drawn through the centrifugal separator during the separation of the nitrocellulose from the nitrating acids, several laboratory experiments are given below.

Table I

Exp. No.	Moisture grains per cu. ft.	Air temp. in wringer	Relative humidity percent	Yield, gms. N/C per gm. cotton linters	Grain	Nitrogen	Remarks
		° C.				*Percent*	
1	6.88	27.5	60	1.23	Very bad	10.91	Wringing cycle extended to 30 mins. to exaggerate conditions. Atmospheric air used in this—normal temperature and humidity prevailing during this test.
2	8.02	25.5	77	1.40	do	11.24	3 min. wringing at prevailing atmospheric conditions.
3	1.48	20.0	21	1.56	Practically none	11.96	Air passed through 3 $CaCl_2$ bottles and finally through concentrated H_2SO_4 before entering wringer.
4	3.39	11.0	77	1.50	do	11.83	The air in this case was drawn from the outside. Normal conditions prevailing for this period of the year.
5	9.30	29.0	75	1.46	Very bad	11.73	Air going into wringer artificially humidified by pumping it through warm water just prior to introduction into wringer.
6	8.06	29.0	65	1.47	do	11.70	Air same as in (5).
7		5.0		1.52	Practically none	11.89	Current of CO_2 from cylinder passed directly into wringer. This gas has moisture content of 0.5 percent.
8	1.32	2.0	55	1.57	do	11.92	Air from outside—normal temperature and humidity for prevailing weather conditions.

In these experiments a standard purified cotton linter was used as the starting material. The linter was dried in an oven to approximately 2% moisture in order to eliminate any variations in results which might be attributed to varying moisture contents. The nitrating acid mix used in each case was:—

HNO_3	22.50
H_2SO_4	58.36
H_2O	19.14

In each experiment 34 grams of the cotton linter were immersed in 1500 grams of the acid mix and agitated for three minutes, the cellulose being allowed to remain in the nitrating acids for a total of 30 minutes. The nitrocellulose thus obtained was then quickly transferred to a slowly rotating aluminum centrifugal separator basket perforated with numerous small holes to permit escape of the acid. The centrifugal separator was speeded up to approximately 1800 R. P. M. and the charge run for three minutes. The force draft was introduced through the cover of the outside casing of the separator, carrying the acid fumes through an outlet in the side of the casing.

At the end of the wringing cycle the charge was quickly quenched and then stabilized by boiling in water followed by hot water washes in accordance with practice well known in the art. In the washing process and for the change of water for the boiling treatment the nitrocellulose was poured into a Buchner funnel and the fines retrieved by filtering the wash water through a matte filter of the nitrocellulose itself. This procedure not only provides more accurate data for yield determinations, but also insures a more representative final solution. The nitrogen contents given in the following table were determined according to methods described in A.S.T.M. Specifications, Designation D-301-31T.

"Grain" was determined by means of a spatula, following the procedure described heretofore, where a fan-shaped drip is produced and a quantitative measurement made by looking through this drip. The solutions for this test were made up according to the method described in A.S.T.M Specifications, Designation D-301-31T, Formula A, for viscosity determinations; in some cases where the presence of grain is not readily observed in the more dilute solution of Formula A, Formula B may be used.

The nitrocellulose produced according to Experiment No. 1 gelled badly in solution, indicating that the nitrocellulose had taken up the solvents but had not dispersed in them. Especially high turbidity was noted and graining was excessive, as was also true of the solution prepared from the nitrocellulose produced according to Experiment No. 2.

In these experiments the velocity of the air going through the centrifuge was approximately 1.5 to 2.0 cubic feet per minute.

An additional experiment was conducted on a plant scale whereby excessive humidity was produced by closing up the centrifuging room and opening steam lines. In this way the temperature was raised to 75° F. and the relative humidity to about 95%. The moisture content of the air going into the centrifuge was then about 9.0 grains per cubic foot, the centrifuging being continued for three minutes with air being supplied at a rate of 700 cubic feet per minute. Samples taken from the exposed surface of the acid wet nitrocellulose cake at the conclusion of the centrifuging cycle and made up into solutions showed

excessive grain. The steam lines were then closed and the doors and windows of the centrifuging room opened to provide weather conditions prevailing at that time. The temperature dropped to 53° F. and the relative humidity to 55%. The moisture content of the air under these conditions is about 3.4 grains per cubic foot. Samples taken from the exposed surface of the acid wet nitrocellulose cake at the completion of the centrifuging cycle and made up into solutions showed practically no grain, thus confirming the laboratory scale test.

As the result of numerous tests it has been found that the moisture content of the air, or other inert gas, should not exceed substantially 5 grains per cubic foot in order to secure acceptable solutions with respect to graining, unless the centrifuging period is materially decreased or the amount of air supplied to the centrifuge is decreased, or both. Since saturated air at 55° F. contains about 5 grains of air per cubic foot of gas, it will be seen that where the acid wet nitrocellulose is not exposed to temperatures above 55° F. graining difficulties will not be encountered and the present invention is only useful where operations are carried out at temperatures above 55° F.

As previously stated, applicant has definitely found that the graining characteristic of nitrocellulose is directly caused by exposing the acid wet nitrocellulose to moisture, and it naturally follows that by reducing the amount of air passing through the acid wet nitrocellulose there is less opportunity for the nitrocellulose to pick up moisture, and therefore less tendency for the nitrocellulose to show graining characteristics. By altering plant scale equipment to reduce materially the draft necessary to carry off the fumes from the centrifuge, and also by reducing the time of centrifuging, normally in the neighborhood of three minutes, the graining tendency can be reduced, although such means will not eliminate graining where there is a high moisture content in the air. However, by taking such precautions, the graining tendency can be reduced materially even though the moisture content of the air be not reduced as low as five grains of water per cubic foot of air. Therefore, the present invention comprises, in a broader phase, the step of reducing the graining characteristic of nitrocellulose, where the humidity of the atmosphere exceeds five grain of water per cubic foot of air, by at least partially dehumidifying the air supplied to the centrifugal separator, even though the air is not necessarily dehumidified to such an extent that it contains less than five grains of water per cubic foot.

In the experiments described above, the air was dehumidified by passing through calcium chloride bottles and concentrated sulphuric acid, but it is to be understood that on a plant scale various commercial dehumidifying apparatuses would be suitable, such as the silica gel dehumidifiers now used for dehumidifying air in steel plants. Obviously economies in the dehumidifying operation will be effected by reducing the draft of air through the centrifuges, or reducing the time for centrifuging. However, a sufficient draft is necessary to carry off the fumes and incomplete centrifuging may not be economical, due to high acid losses which may occur.

In the foregoing table, it will be noted that not only does the use of a dehumidified gas give a certain method of eliminating the graining characteristic, but also there is less denitration and an increased yield. A number of tests show around a 5% increase in the yield where the air contains less than 5 grains of water per cubic foot, other variables remaining constant.

The present invention is broadly applicable to nitrocellulose made from any raw material and employing any nitrating acid mix. The invention is likewise applicable regardless of the method by which the air or inert gas is dehumidified. This may be done simply by artificially cooling the warm moist air below its dew point to cause precipitation of water before the air is led into the centrifuge.

Particularly on days of abnormally high temperature and humidity it is also advantageous to arrange to use air or other gas of low moisture content in removing acid fumes from the nitrating dippers and, in fact, keeping the acid wet nitrocellulose in an atmosphere of dehumidified gas right up to the point where it is drowned in water, although as hereinbefore stated, under most conditions it is sufficient to dehumidify the air being forced into the wringer.

It will thus be seen that by the present invention a process has been devised whereby the presence of grain in nitrocellulose solutions may be consistently and entirely eliminated or reduced to a minimum not noticeable in practical uses of nitrocellulose solutions. Furthermore, the present invention provides a process whereby the yields of nitrocellulose may be increased from 2–6% by avoiding losses attendant upon the factors which cause the formation of soluble products in nitrocellulose, characterized by the presence of grain in solutions made from nitrocellulose. Further, denitration tendencies are eliminated or greatly minimized according to the process of the present invention. By the present invention, manufacturers of nitrocellulose are enabled to consistently produce high quality nitrocellulose throughout the year, whereas heretofore, operating under conditions of high temperature and humidity such as frequently occur during the summer months in the temperate zones, the nitrocellulose varied widely with respect to the graining characteristics and frequently would be unacceptable to many users of the nitrocellulose. In other words, the present invention provides a process which permits the manufacture of a nitrocellulose of uniform quality, regardless of prevailing weather conditions.

I wish it to be understood that I do not desire to be limited to the exact details shown and described, except as defined in the appended claims, for obvious modifications will occur to a person skilled in the art.

I claim:

1. In the preparation of nitrocellulose where the humidity of the atmosphere exceeds five grains of water per cubic foot of air, said preparation comprising treating cellulose with nitrating acids, centrifuging to separate the nitrating acids, and then drowning the nitrocellulose thus obtained in water, the step which comprises maintaining the nitrocellulose in an inert gas having less than five grains of water per cubic foot of gas during the separation of the nitrating acids and until the nitrocellulose is drowned in water.

2. In the preparation of nitrocellulose where the humidity of the atmosphere exceeds five grains of water per cubic foot of air, said preparation comprising treating cellulose with nitrating acids, separating the nitrating acids from the thus obtained nitrocellulose by means of a cen-

trifugal separator, and then drowning the nitrocellulose in water, the step which comprises supplying an inert gas having less than five grains of water per cubic foot of gas to the centrifugal separator during the acid separation.

3. In the preparation of nitrocellulose where the humidity of the atmosphere exceeds five grains of water per cubic foot of air, said preparation comprising treating cellulose with nitrating acids, centrifuging to separate the nitrating acids, and then drowning the nitrocellulose thus obtained in water, the step which comprises maintaining the nitrocellulose in air having less than five grains of water per cubic foot of air during the separation of the nitrating acids and until the nitrocellulose is drowned in water.

4. In the preparation of nitrocellulose where the humidity of the atmosphere exceeds five grains of water per cubic foot of air, said preparation comprising treating cellulose with nitrating acids, separating the nitrating acids from the thus obtained nitrocellulose by means of a centrifugal separator, and then drowning the nitrocellulose in water, the step which comprises supplying air having less than five grains of water per cubic foot of air to the centrifugal separator during the acid separation.

5. In the preparation of nitrocellulose where the humidity of the atmosphere exceeds five grains of water per cubic foot of air, said preparation comprising treating cellulose with nitrating acids, separating the nitrating acids from the thus obtained nitrocellulose by means of a centrifugal separator, and then drowning the nitrocellulose in water, the step which comprises reducing the graining characteristic of the nitrocellulose by at least partially dehumidifying the air supplied to the centrifugal separator during the acid separation.

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