Patented June 14, 1949

2,473,473

UNITED STATES PATENT OFFICE

2,473,473

METHOD OF PREPARING REGENERATED CELLULOSE

Gordon D. Hiatt and Carlton L. Crane, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application February 5, 1945, Serial No. 576,364

5 Claims. (Cl. 106—168)

1

This application relates to the preparation of regenerated cellulose products in which low viscosity cellulose is dissolved in a mixture of N_2O_3 and N_2O_4 at a temperature below the boiling point of N_2O_3. This solution is employed for the preparation of the regenerated products.

Regenerated cellulose products have previously been prepared by converting cellulose to, for instance, the xanthate form and then coating out onto a film-forming surface. Nowhere in the prior art has it been previously recognized that nitrogen oxides are suitable for use for this purpose, forming regenerated cellulose sheets or filaments having good transparency.

Cellulose has previously been treated with NO_2 or its dimer N_2O_4, but in those cases the primary object was the enhancing of the reactivity of the cellulose and no dissolving of the cellulose was desired, or obtained. In other cases, cellulose has been treated with NO_2 and an oxidized or a nitrated product has been obtained.

One object of our invention is to provide a method of preparing regenerated cellulose using nitrogen oxides. Another object of our invention is to provide a method of preparing regenerated cellulose showing good clarity, using nitrogen oxides in which the final product contains less than 1% nitrogen and shows no oxidized characteristics. Other objects will appear herein.

We have found that cellulose having a viscosity of less than 200 centipoises, preferably 2–50 centipoises, may be readily dissolved in a mixture of N_2O_3 and N_2O_4 at a temperature not to exceed 37° F. and that the thus formed solution may be coated out onto a film-forming surface, thereby forming sheets of regenerated cellulose. We have found that filaments of regenerated cellulose may be prepared by forming a cellulose solution in nitrogen oxides as specified and then extruding the solution such as into a precipitating bath or into air to form filaments or fibers of rayon or synthetic yarn.

The cellulose which is dissolved in accordance with our process may be any low viscosity cellulose material, this feature of our invention being critical. If the cellulose material is of medium or high viscosity, such as, acetylation grade cotton linters, or the like, it is necessary that the viscosity be reduced in some manner. This may be accomplished by treating the cellulose with a mixture of acetic and sulfuric acids for a time. For instance, one part of the cellulose mixed with three parts of acetic acid and .09 parts of sulfuric acid, is allowed to mix for a sufficient time to reduce the viscosity of the cellulose to the desired point. Ordinarily, mixing for 4 hours

2

at 100° F. is sufficient to obtain a viscosity below 200 centipoises. However, the time and temperature necessary depend upon the amount of viscosity reduction which is desired. Oftentimes, in the refining of cellulose materials, severe treatments are employed, and, in those cases, the refined cellulose may be employed directly without any preliminary treatment thereof. In some cases, we prefer to add sufficient alkaline earth salts such as $MgCO_3$, MgO or $CaCO_3$ to effectively neutralize the catalyst present, in this example sulfuric acid. If desired, an alkali metal salt of a weak acid such as sodium bicarbonate may be employed for this catalyst neutralization.

The liquid in which the cellulose is dissolved should be one containing both N_2O_3 and N_2O_4, at a temperature not to exceed 37° F. Although in practical operation, a temperature within the range of 26–28° F. is quite suitable, nevertheless, temperatures lower than this may be employed, the criterion being that the solution remain liquid at the temperature used.

The dissolving mixture of N_2O_3 and N_2O_4 may be made in either of two ways:

1. By mixing the oxides themselves. Mixtures which are suitable may vary anywhere from a composition of 97% N_2O_4 and 3% N_2O_3 to 10% N_2O_4 and 90% N_2O_3. Cellulose which will not dissolve in either of these oxides by themselves will dissolve in any mixture of the two oxides within the range stated.

2. By incorporating a small amount of water in liquid N_2O_4 at a temperature not to exceed 30° F. In mixing water with the N_2O_4, it is necessary to use care so that the temperature is kept down, thus preventing the loss of N_2O_3. The amount of water which would be mixed with the N_2O_4 should be limited, the upper limit being not more than 20% including the water in the cellulose which is to be treated. Ordinarily, an amount of water not exceeding 10% of the N_2O_4 would be mixed therewith. Above this proportion, there is danger of causing oxidation of the cellulose, so that the desired product may not be obtained. In order to form a mixture suitable for dissolving cellulose, it is necessary that at least 0.5% of water be incorporated in the N_2O_4.

After forming the dissolving mixture of nitrogen oxides, low viscosity cellulose, as prescribed herein, is mixed therewith, ordinarily in the proportion of from 1% up to 8–10% and even as high as 20% of the dissolving solution, the proportion of cellulose dissolved depending upon its viscosity. For instance, with a cellulose having a viscosity of 2–12 centipoises, a solution on the order of 3–20% may be formed and will be useful

for forming regenerated cellulose. With cellulose having a viscosity in the upper portion of the range given (150–200 centipoises), it is desirable to dissolve approximately 1–5% of cellulose in the dissolving solution to obtain a solution of the best fluidity for use. It is usually desirable in practical operation in dissolving the cellulose to also employ an inert solvent either adding the solvent after the solution has taken place, or diluting the solvent mixture with the diluent. Acetic acid has been found to be well suited for this purpose and as much as 9 parts of acetic acid per part of N_2O_4 may be used. However, various other solvents, such as methylene chloride, isopropyl ether, tetrachlorethane, chloroform, propylene chloride, trichloroethylene or ethylene chloride may be used.

To make regenerated cellulose sheeting in accordance with our invention, the cellulose of the viscosity given is added to the dissolving medium which is kept at a temperature of 26–37° F. or below. Upon stirring, the cellulose almost immediately dissolved and is coated out directly at this temperature onto glass plates cooled to about 25° F. The cooling prevents the solvents from evaporating too rapidly thereby preventing bubbling in the layer and allowing gel formation. The setting or gelling may be accomplished, for instance, by subjecting the coating to a draft of air for a short time such as 5 minutes. During this interval, the coating sets or gels, and may then be immersed in water. After treatment therewith, the coating may be stripped from the plate and washed to remove all traces of acid therefrom. Broadly, the formation of the regenerated cellulose sheet is accomplished by coating a solution, preferably one in which the inert solvents have also been used, onto a film-forming surface, causing the coating to set and then washing to remove acid or other water-soluble material therefrom. In cases where an inert diluent is employed, setting of the coating takes place more readily than in those cases where the sheet is coated out from a solution of the cellulose using only nitrogen oxides as solvents. If desired, the washing baths for the regenerated cellulose sheet may be a counter current system involving acetic acid and water. We have found that the initial use of an acetic acid bath facilitates the curing operation in forming the finished sheet. It is also desirable in the final wash to incorporate a small amount of water-soluble material which acts as a plasticizer in the sheet, for instance, some water-soluble polyhydric material which acts as a humectant, such as glycerin or a glycol.

Cellulose dissolved in mixtures of N_2O_3—N_2O_4 in accordance with our invention is found when regenerated therefrom not to have been oxidized nor is the nitrogen content thereof increased to any substantial extent. For instance, cellulose was dissolved in a mixture of N_2O_3 and N_2O_4, and one-half of the solution formed was immediately regenerated by pouring the solution into distilled water. The remaining portion was held for 66 hours in a Dry Ice bath and was then regenerated. The materials were dried and gave the following analyses:

Time	Carboxyl	Nitrogen
Hours	*Per cent*	*Per cent*
0	.15	.22
66	.23	.40

If solutions of cellulose in accordance with our invention are allowed to stand for prolonged periods of time, loss of nitrogen oxides occurs, depending upon the temperature at which the solution is kept. If the solution is kept at a temperature above 40° F., this loss is fairly pronounced, and gelling will take place within a short time. If, however, the temperature is below 40° F., the loss of nitrogen oxides is more gradual depending upon the temperature at which the solution is kept. Therefore, if the solutions are to be kept for some time, it is desirable that it be at a temperature below 30° F., such as 26–28° F. or below, to avoid gelling.

If a solution has gelled, it may be redissolved by adding nitrogen oxides thereto, particularly N_2O_3 or a mixture of N_2O_4 with some water therein.

The solutions of cellulose obtained in accordance with our invention are extremely clear and brilliant, and no fibers can be discerned therein either in the sunlight or in polarized light. Any dirt or insoluble matter can be easily removed therefrom by filtering these dopes, such as through glass filter cloth. Sheets formed from solutions in accordance with our invention give tensile strengths comparable to that of sheets of cellulose regenerated from the xanthate.

The following examples illustrate our invention:

Example 1

Sixty parts of cellulose having a cuprammonium viscosity of 5 centipoises were added to a mixture of 402 parts of acetic acid, 18 parts of water, and 180 parts of N_2O_4, all at a temperature of 28–30° F. The mass was stirred while maintaining the restricted temperature until a uniform, brilliant, clear solution was formed. The solution was coated onto a glass plate to form a sheet having .013 inch thickness, and the film or sheet allowed to stand in a draft of air for 5 minutes. The film was then immersed in glacial acetic acid for 5 minutes. The film was then washed free from acid with water and immersed in a 3% glycerin solution for 15 minutes. An alternative washing method is that of immersing the air-treated film directly in water. The wet film was dried on a smooth, metal surface to give a clear, flexible film of .001–.0013 inch thickness. The dry product analyzed within the following ranges:

	Per cent
Nitrogen	.04–.06
Carboxyl	0.2–0.5

These films when freshly coated are somewhat resistant to wetting with the wash water. To improve the susceptibility to water and aid in reducing the washing time, it has been found advantageous to use wetting agents, such as ordinary soap, Triton K–60, or Tergitol 4. As far as can be determined, these wetting agents have no deleterious effects on film regenerated from nitrogen oxide solutions.

Example II

Two hundred fifty parts of refined cotton linters having a moisture content of 8.75 parts and an ash content of .03 part was treated with 750 parts of acetic acid and 16½ parts of 95% sulfuric acid for 4 hours at 100° F. in a Werner-Pfleiderer-type mixer. This treatment reduced the cuprammonium viscosity of the cellulose to well below 200 centipoises. Five hundred parts of the mixture thus obtained were added to 656 parts of N_2O_4, 66 parts of water, and 768 parts of acetic acid, all at a temperature of 28–30° F.

The mixture was stirred while maintaining the temperature at 28–30° F. until the cellulose dissolved and formed a clear green-blue viscous uniform solution. The solution was cast as a thin layer onto a glass plate, forming a film or sheeting of .013 inch. This film was allowed to stand in a draft of air for 5 minutes and was then washed in water until free from acid and transferred to a water bath, containing sufficient magnesium carbonate to give an initial pH value of 9.3. The film or sheeting was then immersed in 3% glycerin solution and was dried. The 656 parts of N_2O_4, 66 parts of water, and 768 parts sheeting was tested by heating for 4½ hours at 160° F. using commerical sheeting as the control. The film or sheeting prepared in accordance with the above example exhibited only a light color and was clear, whereas the sample of commerical sheeting developed more color than did the formed sample.

Example III

Nine hundred forty-six parts of cotton linters having a 2½ cuprammonium viscosity of 7.8 centipoises was added to a mixture of 394 parts of water, 4000 parts of N_2O_4, and 16,000 parts of acetic acid. The N_2O_4 employed here was a portion of the red-brown upper layer of an N_2O_4–HNO_3 equilibrium mixture, this means being employed to refine the N_2O_4. The temperature of the liquid mixture used and of the entire mass during the reaction was maintained at 28–30° F. Upon stirring, a uniform green-blue viscous solution was obtained which was regenerated by casting into sheets. In this example as in the preceding one, the temperature was maintained at the reduced range over the entire course of the dissolving operation.

Example IV

Nine hundred forty-six parts of cellulose having a 2½% cuprammonium viscosity of 7.8 centipoises was added to a mixture having a temperature of 20–30° F., which mixture consisted of 159 parts of water, 8000 parts of N_2O_4 and 2000 parts of acetic acid. The temperature of 28–3° F. was maintained while stirring until a clear green-blue viscous uniform solution was obtained. This solution was cast into films, the films washed, plasticized and dried, to form clear, flexible foils.

Example V

Sixty parts of cotton linters having a 2½ cuprammonium viscosity of 7.8 centipoises was mixed with a liquid mixture previously cooled below 30° C., consisting of 402 parts of acetic acid, 180 parts of N_2O_4, and 18 parts of water. The mass was mixed while maintaining the temperature until a clear green viscous liquid was obtained. The solution was coated out in the form of films of .0011 inches and were analyzed for carboxyls and nitrogen contents. When analyzed, these films showed the following values:

	Per cent
Carboxyl	0.124
Nitrogen	0.18

Example VI

Two hundred fifty parts of commercial cotton cellulose were treated with a mixture of 750 parts of acetic acid and 16.56 parts of 95% sulfuric acid for 4 hours at 100° F. in a Werner-Pfleiderer-type mixer, this treatment reducing the viscosity of the cellulose well below 200 centipoises. Four hundred parts of this treated material was mixed with a mixture of 450 parts of N_2O_4, 45 parts of water, and 705 parts of acetic acid and the mass was stirred until a clear green or blue solution was obtained. The solution was held for 24 hours at 26.28° F. and the cellulose was regenerated by pouring the solution into a bath of 90% methyl alcohol. The product was washed free of acid with 90% methyl alcohol and dried, the dried product analyzed 0.3% nitrogen. The same procedure was repeated using 400 parts of the preheated cellulose except that a mixture of 10 parts of magnesium carbonate and 200 parts of acetic acid was first added to the pretreated cellulose and mixed in prior to its treatment with the acetic acid solution of N_2O_4. The dried product analyzed 0.06% nitrogen.

The viscosity values for cellulose as used herein refer to the viscosity of the cellulose in a 2½% cuprammonium solution as is ordinarily known and employed in the cellulose art for determining the viscosity of cellulose. This test is designated as Technical Association Method T–206–m–37 in the literature on cellulose. The N_2O_4 which may be employed in dissolving cellulose in accordance with my invention may be obtained from the usual sources for obtaining oxides of nitrogen, such as by the action of nitric acid on metals, such as copper, the reduction of nitric acid, such as by arsenious acid, or the synthetic preparation of NO_2, such as by oxidizing ammonia or by synthesizing these oxides directly from nitrogen and oxygen. It is usually desirable to employ N_2O_4 of a refined type. The nitrogen dioxide gas formed by one of the reactions specified may be collected by passing it through a brine-cooled condenser into a refrigerated container or flask cooled with solid carbon dioxide.

N_2O_3, such as is suitable for use in forming dissolving mixtures in accordance with our invention, is conveniently prepared by treating commercial sodium nitrite with 95% sulfuric acid. The sulfuric acid may be slowly mixed with the sodium nitrite, N_2O_3 gas coming off and being collected by means of a brine-cooled condenser and a refrigerated flask, such as mentioned for use in collecting N_2O_4. The N_2O_3 is thereby collected in the form of a bluish liquid.

It is desirable when cellulose is pretreated with a mixture of acetic acid and sulfuric acid to prepare it for treatment in our process that the cellulose be treated with the magnesium salt of a weak acid, such as magnesium carbonate, prior to the treatment with N_2O_4. We have found that this procedure reduces the amount of combined nitrogen introduced into the cellulose in solution in the process and Example VI is for the purpose of illustrating that effect by repeating the same procedure only employing magnesium carbonate therein. Instead of magnesium carbonate, some other neutralizing magnesium compound may be employed, such as magnesia itself, its hydroxide or the salt of a weak acid.

We claim:

1. A method of preparing regenerated cellulose which comprises mixing together at a temperature not to exceed 37° F. cellulose having a viscosity not to exceed 200 centipoises, N_2O_4, an inert solvent compatible with N_2O_4 containing between 0.5 and 20% of water, and 0.5–20% of water, based on the weight of the N_2O_4, until solution of the cellulose occurs, followed by imparting a physical form to the solution and setting the so-formed solution.

2. A method of preparing regenerated cellulose which comprises mixing together at a tempera-

ture not to exceed 37° F. cellulose having a viscosity not to exceed 200 centipoises, N_2O_4, an inert solvent compatible with N_2O_4 containing approximately 10% of water, based on the weight of the N_2O_4, until solution of the cellulose occurs, followed by setting a film of the solution upon a film-forming surface.

3. A method of preparing regenerated cellulose which comprises mixing together at a temperature not to exceed 37° F. cellulose having a viscosity not to exceed 200 centipoises, N_2O_4, acetic acid, and 0.5–20% of water, based on the weight of the N_2O_4, until solution of the cellulose occurs, followed by imparting a physical form to the solution and setting the so-formed solution.

4. A method of preparing regenerated cellulose, which comprises mixing together at a temperature not to exceed 30° F. cellulose having a viscosity not to exceed 200 centipoises, N_2O_4 acetic acid and 0.5–20% of water, based on the weight of the N_2O_4 until solution of the cellulose occurs

followed by setting a film of the solution upon a film-forming surface.

5. A method of preparing regenerated cellulose which comprises mixing together at a temperature not to exceed 37° F. cellulose having a viscosity not to exceed 200 centipoises, N_2O_4, acetic acid, and approximately 10% of water, based on the weight of the N_2O_4, until solution of the cellulose occurs, followed by setting a film of the solution upon a film-forming surface.

GORDON D. HIATT.
CARLTON L. CRANE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,939,235	Staud	Dec. 12, 1933

Certificate of Correction

Patent No. 2,473,473. June 14, 1949.

GORDON D. HIATT ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 13, Example II, strike out "656 parts of N_2O_4, 66 parts of water, and 768 parts"; line 45, Example IV, for "28–3° F." read *28–30° F.*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of November, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.