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PREPARATION OF SOLUBLE NITROCELLULOSE HAVING CARBOXYL GROUPS IN THE PRIMARY POSITION

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This invention relates to acetone-soluble cellulose nitrates having carboxyl groups in the primary position and their preparation.

One object of my invention is to provide a cellulosic material having both a nitrate content and a carboxyl content which material is soluble in acetone. Another object of my invention is to provide a process of preparing an acetone-soluble cellulose nitrate having carboxyl groups in the primary position. A further object of my invention is to provide a cellulosic material which will adhere to the surfaces of both cellulose nitrate and of organic acid esters of cellulose and is also reactive with basic materials. Other objects of my invention will appear herein.

I have found that cellulose oxidized with NO_2 (or its dimer, N_2O_4) as described in Yackel and Kenyon Patent 2,232,990 or in Kenyon and Yackel Patent No. 2,448,892, when nitrated and then steeped in dilute aqueous alkali, gives cellulosic material which is acetone soluble, is adherent to either cellulose nitrate or organic acid esters of cellulose when applied thereto from solution in a volatile solvent or when its esters are applied to the cellulosic material, and is susceptible to basic materials.

The cellulosic material of my invention is prepared by first oxidizing cellulose with NO_2 or N_2O_4 so as to impart a carboxyl content of 0.05% to approximately 6% thereto. The degree of oxidation of the cellulose is primarily dependent upon the time of treatment. A time of 1–4 hours of treatment with NO_2 is usually sufficient to give the desired carboxyl content to the cellulose although the carboxyl content achieved may depend to some extent on the rate of application of the NO_2 to the cellulose. If the cellulose is oxidized by treating it with a solution of NO_2 in a solvent such as carbon tetrachloride, the concentration of NO_2 as well as the time is important in determining the carboxyl content attained. For instance, Examples 8 and 9 of Patent No. 2,448,892 show the preparation of oxidized cellulose having a carboxyl content of 0.05% to 6% by means of a low concentration of NO_2 in carbon tetrachloride even though a long time of treatment is employed. This first step of my process is employed in such a manner that only a small carboxyl content is imparted to the cellulose.

The cellulose oxidized as described is then nitrated to obtain a product having a nitrogen content of 10.5–12.2% of nitrogen. The nitrating bath used consists of 80–98% of nitric and sulfuric acids, the remainder being made up principally of water. The HNO_3—H_2SO_4 in the nitrating bath should approximate equal parts (that is, each being 40–60% of their total). The nitration of the oxidized cellulose is carried out to substantial equilibrium with the particular nitrating mixture employed. Ordinarily a time of ½ hour at room temperature is sufficient to obtain complete reaction although longer times of treatment may be employed although serving no useful purposes beyond 30–45 minutes. After the cellulose has been nitrated it is stabilized by subjecting to treatment with hot water although in some cases this hot water treatment may be unnecessary. The cellulose nitrate, however, should be repeatedly washed with mineral-free water, preferably hot (such as 150–212° F.) until all of the nitrating materials have been removed therefrom. After the cellulose material has been thoroughly washed, it is then subjected to treatment with a mild alkaline material in water solution so as to impart acetone solubility thereto. Such materials as calcium acetate, calcium hydroxide, barium hydroxide or sodium hydroxide may be used either at an elevated temperature or at room temperature. The time and concentration of alkali treatment varies depending upon the alkali used. Ordinarily a time of 15 minutes is desirable even under the best conditions although there have been exceptional cases where a time of as little as 5 minutes of treatment of the cellulosic material with alkali solution has imparted acetone solubility. If sodium hydroxide is employed, a concentration within the range of .01 to 0.4% should be employed and a temperature of 40° C. may be used. If desired, however, room temperature may be employed with good effect. If barium hydroxide is used, it is desirable to employ a concentration within the range of 0.1% to 3% and a temperature of 40° C. to obtain acetone solubility although here again room temperature will be set. With calcium hydroxide it is desirable to employ a saturated solution thereof although a concentration may fall to as low as 0.1% and still be effective in imparting acetone solubility. With calcium acetate the concentration may be from 0.1% to 10% to impart acetone solubility to the cellulose material being treated. In all of the alkali treatments it is desirable that a temperature at least as high as 10° C. be employed for the treatment. Although a time of 15 minutes is often satisfactory for imparting acetone solubility, usually a steeping for one hour is desirable to assure complete acetone solubility of the

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material being treated. The time of steeping, however, is not critical and may be several hours such as up to 10 hours. Other alkalies, such as sodium carbonate, sodium borate, or the like, may be employed, if desired, for treating the nitrate of oxidized cellulose to impart acetone solubility thereto. The criterion of this reagent is that it be a mild alkali or, if a pronounced alkali, that it be employed in a dilute condition. The alkali used should not be so strong that degradation of the cellulose occurs which would be evidenced by discoloration of the product and decrease of its nitrogen content. After the product has been treated with alkali to impart acetone solubility thereto, it is desirable to wash with acid and then with water to remove all trace of alkali therefrom. A product is thereby obtained which can be dissolved up into acetone and used for coating, such as subbing layers or anti-halation layers for photographic film, situations where susceptibility to dyeing with basic dyes are desired or for adhesive purposes of various types.

The following examples illustrate my invention:

Example 1.—20 parts of dried refined cotton linters having a cuprammonium viscosity of 135–200 centipoises was immersed for 2 hours in a mixture of 80 parts of liquid N_2O_4 and 320 parts of carbon tetrachloride. The material was then separated from the liquid and washed with 13 changes of distilled water until free of the N_2O_4—CCl_4 mixture. The material was dried and was found to contain 3.8% of carboxyl and .33% nitrogen. The oxidized cellulose was then placed in a nitration mixture consisting of 47.2% nitric acid, 47.2% sulfuric acid, the balance being water, and the treatment was maintained for 37 minutes at room temperature (70° F.). The product obtained was washed thoroughly with distilled water until free of acid and then treated with a saturated aqueous solution of calcium hydroxide at 70° F. for 2 hours. This was followed by treatment with 0.5 N HCl for one hour at 70° F. and then by hot (200° F.) distilled water washes until a product was obtained which was free of acid and stable as shown by the German heat test. The product obtained was completely soluble in acetone and contained 12.16% nitrogen and 2.5% carboxyl.

Example 2.—20 parts of oxidized cellulose prepared as in the preceding example was nitrated with a mixture of 41.2% nitric acid, 41.2% sulfuric acid, and the balance water, for 37 minutes at 70° F. The product was washed with distilled water until free of acid and portions thereof were treated by each of three different alkaline media as follows:

A. A portion of the oxidized cellulose nitrate was treated for 2 hours at 70° F. with a 0.5 molar calcium acetate solution. The product was then centrifuged free of excess liquid and immersed in 0.5 N HCl solution for 30 minutes, then washed with hot distilled water until free of acid and was found to possess a stability of at least 25 minutes as determined by the German heat test. The material was dried and was found to be completely acetone soluble and to contain 11.64% nitrogen and 1.08% carboxyl.

B. A portion of the distilled water-washed nitrated material was treated for 2 hours at 70° F. with a 0.1 molar barium hydroxide solution, followed by treatment with HCl and hot distilled water as in A. The sample obtained was completely acetone soluble and was found to contain 11.48% nitrogen and 1.08% carboxyl.

C. In this case a saturated solution of calcium hydroxide was employed as the alkaline medium. A product was obtained completely soluble in acetone and containing 11.55% nitrogen and 1.08% carboxyl.

Example 3.—2 parts of dried refined cotton linters were immersed for 2 hours in a mixture of 1 part N_2O_4 and 4 parts of carbon tetrachloride using a ratio by weight of 1 part of linters to 20 parts of N_2O_4 mixture. The product obtained was washed thoroughly with distilled water until free of the N_2O_4—CCl_4 mixture and was then dried. The carboxyl content of the material was 1.9%. This oxidized cellulose was nitrated at 70° F. for approximately 30 minutes with a nitration bath consisting of 41.25% nitric acid, 41.25% sulfuric acid, and the balance water. The nitrated sample was washed with 0.1 N sodium hydroxide for ½ hour at 70° F. and then with 0.5 N HCl for 10 minutes, followed by washings with hot distilled water until stable as determined by a German heat test of at least 25 minutes. The nitrogen content of the final product was 11.44% and the carboxyl content was 1.4%. This material was dehydrated with n-butyl alcohol and made into a solution having a solids content of 11% using as the solvent a mixture of 9 parts of methyl alcohol and 1 part of acetone. A readily flowable solution was obtained suitable for use for coating paper, fabrics, cellulose ester sheeting, or the like. The material in solution in volatile solvent could also be employed for the preparation of cellulose ester products from which the volatile liquor could be readily evaporated.

The material prepared in accordance with my invention is susceptible to the action of basic dyes and any color desired may be imparted thereto whether after the material has been coated out in the form of a layer or prior to that coating operation. Also, this material may be reacted with bases in order to incorporate ions therein by combining with the carboxyl. For instance, for some purposes it might be desirable to form the copper, zinc, or other metallic salt of this material. If desired, amines may be reacted thereto to incorporate that substituent chemically into the material. Due to this property of chemically combining with cations it is desirable in the final wash thereof that only mineral-free water be employed, as the carboxyl groups of the material which I prepare might otherwise combine with the cations due to the hardness in the water.

I claim:

1. A method of preparing an acetone-soluble cellulose derivative which comprises nitrating an oxidized cellulose having a carboxyl content of .05%–6% on the primary groups of the cellulose with a nitrating bath essentially consisting of a mixture of HNO_3 and H_2SO_4, of 80–98% strength, each acid constituting 40–60% of the total acid present, so as to impart a nitrogen content of 10.5–12.2% thereto an acetone-insoluble and alkali-insoluble product resulting and subsequently treating the so-prepared product with a mild alkali solution whereby substantially complete acetone solubility is imparted thereto.

2. A method of preparing an acetone-soluble cellulose derivative which comprises nitrating an NO_2-oxidized cellulose with a nitrating mixture essentially consisting of a mixture of HNO_3 and H_2SO_4, of 80–98% strength, each acid constituting 40–60% of the total acid present, so as to impart a nitrogen content of 10.5–12.2% thereto an ace-

tone-insoluble and alkali-insoluble product resulting and subsequently treating the resulting product with a mild alkali solution whereby substantially complete acetone solubility is imparted thereto.

3. A method of preparing an acetone-soluble cellulose derivative which comprises nitrating cellulose having a carboxyl content of .05% to 6% on the primary groups of the cellulose with a nitrating bath essentially consisting of a mixture of HNO_3 and H_2SO_4, of 80–98% strength, each acid constituting 40–60% of the total acid present, so as to impart a nitrogen content of 10.5–12.2% thereto an acetone-insoluble and alkali-insoluble product resulting and subsequently soaking the product so obtained in dilute aqueous sodium hydroxide having a concentration of .01–0.4% until a substantially completely acetone-soluble product is obtained.

4. A method of preparing an acetone-soluble cellulose derivative which comprises nitrating cellulose having .05% to 6% of carboxyl on the primary groups thereof with a nitrating bath essentially consisting of a mixture of HNO_3 and H_2SO_4, of 80–98% strength, each acid constituting 40–60% of the total acid present, so as to impart a nitrogen content of 10.5–12.2% thereto an acetone-insoluble and alkali-insoluble product resulting and subsequently treating the so-prepared product with an aqueous solution of calcium acetate having a concentration of .1 to 10% whereby substantially complete acetone solubility is imparted thereto.

5. A method of preparing an acetone-soluble cellulose derivative which comprises nitrating an NO_2-oxidized cellulose with a nitrating bath essentially consisting of a mixture of HNO_3 and H_2SO_4, of 80–98% strength, each acid constituting 40–60% of the total acid present, so as to impart a nitrogen content of 10.5–12.2% thereto an acetone-insoluble and alkali-insoluble product resulting and subsequently soaking the resulting product in an aqueous solution of calcium hydroxide having a concentration from 0.1% up to a saturated solution thereof for a sufficient time to impart substantially complete acetone solubility to the resulting product.

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