

UNITED STATES PATENT OFFICE

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DELUSTERED CELLULOSIC PRODUCT AND
METHOD OF PREPARING SAME

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12 Claims. (Cl. 106—40)

This invention relates to cellulosic structures such as filaments, threads, fabrics, sheets, films, caps, tubing, or the like. More particularly, this invention relates to cellulosic structures of the type just mentioned having a subdued or low luster and/or that are more or less opaque.

In the ordinary methods of preparing cellulosic structures, such as filaments, threads, films, caps, tubing, etc., from viscose, cuprammonium, nitrocellulose cellulose acetates and other cellulosic solutions (without the addition of opaquing and/or low luster-inducing agents to the solutions), the products are transparent or translucent and/or very highly lustrous. For many purposes, transparency, brilliant sheen and luster are not desirable and thus restrict the uses of the materials. Recently, various methods have been proposed for producing cellulosic structures having a low or subdued luster and/or opacity.

I have found that I can produce cellulosic structures characterized by a low luster and/or opacity by incorporating therein a highly insoluble, difficultly saponifiable metallic salt of an organic acid of the character described in detail hereinafter which imparts opacity and/or low luster by remaining in the cellulosic structure.

An object of the invention comprises the production of new opacified and/or low luster cellulosic structures. A further object of the invention relates to the production of novel cellulosic structures containing organic compounds which remain in the finished article and which impart opacity and/or low luster. Other objects of the invention will appear hereinafter.

The objects of the invention are accomplished in general by incorporating in the cellulosic solution from which the structure is to be produced an opaquing and/or a low luster-inducing agent of the type hereinafter more fully described.

The opaquing and/or low luster-inducing agent contemplated by the invention is a highly insoluble, difficultly saponifiable metallic salt of a carbocyclic or heterocyclic acid highly deficient in hydrogen and which has a refractive index at least 0.1 above that of the cellulosic medium in which it is to be used. The acid group may be a carboxylic, thiocarboxylic, sulfonic or phosphonic acid group capable of yielding hydrogen ions, providing only that their metallic salts are substantially insoluble, stable and white.

So far as the instant invention is concerned, each closed chain of carbon or hetero-atoms or combination of carbon and hetero-atoms will be considered a nucleus. Thus, benzene, naph-

thalene and carbazole have one, two and three nuclei respectively.

These opaquing and/or low luster-inducing agents, which are preferably white in color, possess a sufficiently low vapor pressure and are sufficiently inert to resist the change or removal from the cellulosic structure in the ordinary process of making and finishing the same during the manufacture thereof. They also effectively resist removal or change during any of the usual processes to which the finished cellulosic structure may be subjected, such as boiling-off, dyeing, bleaching, washing, ironing, etc. These substances are incompatible with the mass of the substance constituting the final product. They may be soluble, but, in the preferred embodiment of this invention, they are insoluble in the solution from which the structure is prepared.

Highly effective delusterants function in particular by reason of their opacifying power which is a function of the difference in refractive index between the delusterant particle and the surrounding medium. Those in my preferred range differ from the index of the medium by at least 0.10 and the greater this difference, the more effective the compound as an opacifier and/or delusterant. Most organic compounds have several indexes and the statement just made refers to the highest index of the compound or to any one of the several indexes.

As illustrative examples of salts of cyclic organic acids coming within the scope of the present invention are the following:

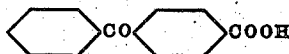
The barium or lead salt of

Phthalic acid



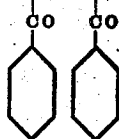
The silver salt of

p-Benzoyl benzoic acid



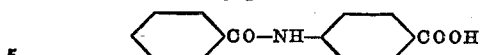
The barium salt of

2,3, Dibenzoyl amino propionic acid



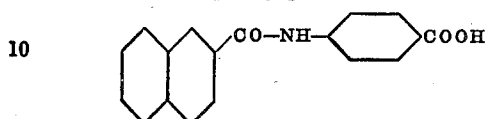
The barium or calcium salt of

Benzoyl-p-amino-benzoic acid



The barium or calcium salt of

Beta-naphthoyl-p-amino benzoic acid



The lead salts of:

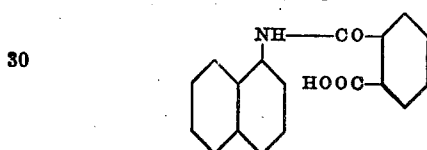
15 Phthalamic acid



N-Phenyl phthalamic acid

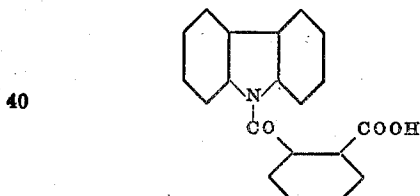


N-alpha-naphthyl phthalamic acid



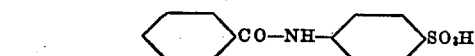
and

35 N-Diphenylene phthalamic acid



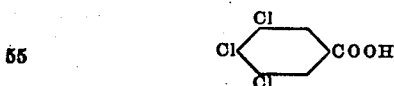
45 The calcium salt of

Benzoyl p-amino benzene sulfonic acid



The calcium salt of

3, 4, 5-Trichloro benzoic acid



The barium salt of

p-Phenyl benzoic acid



Organic compounds of the character described which have a relatively high index of refraction and which are preferred on the basis of cost, color stability, acid insolubility and effectiveness are the following:

Ba or Ca salt of benzoyl P-aminobenzoic acid

Ba or Ca salt of naphthoyl P-aminobenzoic acid

70 Lead salt of phthalic acid

Lead salt of phthalamic acid

Lead salt of N-phenyl phthalamic acid

The quantity of the low luster-inducing and/or opaquing agent which may be used may vary within wide limits, depending principally upon

the opaquing and luster desired in the final product. Cellulosic structures containing these low luster-inducing and/or opaquing agents in amounts ranging from 0.10 to 20.0% by weight have given satisfactory results, but, of course, it is obvious that smaller or larger quantities may be employed as desired. When a viscose solution is employed, satisfactory results may be secured if it contains 7% cellulose and from 0.01 to 1.5% more or less of the low luster-inducing and/or opaquing agent.

If desired, the low luster-inducing agents contemplated by the instant invention may be used in combination with each other and/or with other low luster-inducing agents such as mineral oil, petroleum jelly, waxes, paraffin, benzene, toluene, pine oil or inorganic pigments such as titanium oxide, lithophone, zinc sulfide, etc.

The low luster-inducing agent may be added to the solution at any stage in the course of the manufacture thereof, or after the preparation of the solution and prior to the spinning, extrusion or casting operation. It may be added directly, if the particle size is satisfactory, or after suitable adjustment of the particle size by any of the well known methods such as emulsification, grinding in a colloid mill or pebble mill, or in the form of a suspension or emulsion prepared with or without the assistance of suitable dispersing agents or protective colloids, such as soaps, sulfonated oils, alkyl naphthalene sulfonates, sodium caseinate, etc., or combinations thereof.

In order to more fully explain the principles of this invention, the following illustrative examples are given:

Example I.—The lead salt of N-phenyl phthalamic acid is precipitated in a finely divided form by adding a solution of lead acetate to a solution of the ammonium salt of N-phenyl phthalamic acid. The precipitate is filtered off and dried. The finely divided salt is then dispersed by grinding in a pebble mill with an equal quantity of 2% cellulose acetate dissolved in acetone. The resulting dispersion is incorporated in a 24% cellulose acetate solution in such proportion that 1 part of the lead salt is present for each 10 parts of cellulose acetate. The resulting cellulose acetate solution is dry spun in the usual manner to produce cellulose acetate rayon. The product has a desirable opacity and low luster.

Example II.—The barium salt of benzoyl-p-aminobenzoic acid is ground in an equal weight of acetone in a pebble mill until all the particles have been reduced to about 4 microns or less in diameter. The resulting dispersion is used in making up cellulose acetate solution for dry spinning in the manner described in Example I. It is spun in the usual manner and is found to have a desirable opacity and low luster.

Example III.—A sample of viscose rayon is impregnated with 15 parts of a 20% solution of lead acetate for a period of 1 hour. The rayon is then centrifuged and finally immersed in a saturated solution of phthalic acid at 70–90° C. Lead phthalate is precipitated within the rayon. It is thoroughly washed and dried and is found to have a desirable opacity and low luster.

It is to be understood that these examples do not in any way restrict the invention thereto but merely illustrate several specific and preferred embodiments which have given satisfactory results.

Though the preferred embodiments of this invention contemplate the incorporation of the

low luster-inducing agent in the solution at some time prior to the extrusion or casting thereof, satisfactory results may be secured also by applying the low luster-inducing agent to a previously formed cellulosic structure as for example in the manner described in Example III. In other words, the low luster-inducing agent may be incorporated in the final cellulosic structure by an after-treatment.

Though the invention has been specifically described in connection with the cellulose acetate process, it is obvious that the principles thereof are equally applicable to the viscose, cuprammonium cellulose, cellulose nitrate, and similar processes. It is only necessary that a suitable choice of organic acid salt be made so that the required refractive index is obtained and that the solubility characteristics thereof do not interfere.

It has already been pointed out that the low luster-inducing substance must be incompatible with the mass of substance constituting the final product. In addition, in the case of cellulose acetate or nitrate spinning solutions, it is preferable that the low luster-inducing substance be insoluble in the solvent employed. However, resinous materials and certain crystallized substances, soluble in the solvent, precipitate (on the evaporation of the solvent) in the cellulose acetate in the form of fine amorphous or crystalline particles sufficiently small and well distributed to avoid harmful effect on the physical properties of the resulting structure. The advantage in such cases lies in avoiding the necessity for emulsifying or grinding the compounds to obtain suitable subdivision. Suitable compounds may be readily selected from any specific system by one skilled in the art.

While the invention has been described generally with respect to the use of the various compounds mentioned herein the opaquing cellulosic structures prepared by casting and/or spinning methods, it is desired to emphasize the fact that these compounds are of special benefit in the spinning of artificial silk. Thus, undelustered artificial silk has a shade and luster which is undesired for a great many purposes. In accordance with the present invention, it is possible to produce artificial silk, particularly of the regenerated cellulose type prepared from viscose or cuprammonium cellulose, having a pleasing dull appearance, the dullness being of any degree desired, in which the opaquing and/or delustering agent is uniformly distributed and which does not interfere with the tenacity of the yarn to any large extent.

Since it is obvious that various changes and modifications may be made in the above description without departing from the nature or spirit thereof, this invention is not restricted thereto except as set forth in the claims.

I claim:

1. Artificial cellulosic films, filaments and the like, containing an incompatible, finely divided opacifying and/or delustering agent comprising a salt of a polyvalent metal and an acid of the group consisting of benzoyl p-aminobenzoic acid, naphthol p-aminobenzoic acid, phthalic acid, phthalamic acid and n-phenyl phthalamic acid.

2. Artificial cellulosic films, filaments and the like, containing an incompatible, finely divided opacifying and/or delustering agent comprising a salt of a polyvalent metal and n-phenyl phthalamic acid.

3. Artificial cellulosic films, filaments and the like, containing an incompatible finely divided opacifying and/or delustering agent comprising a salt of a polyvalent metal and benzoyl-p-aminobenzoic acid.

4. Artificial cellulosic films, filaments and the like, containing an incompatible, finely divided opacifying and/or delustering agent comprising a salt of a polyvalent metal and phthalic acid.

5. An artificial thread comprising a cellulosic material having opacity and/or low luster imparted thereto by the incorporation therein of an incompatible, finely divided substance comprising a salt of a polyvalent metal and an acid of the group consisting of benzoyl p-aminobenzoic acid, naphthoyl p-aminobenzoic acid, phthalic acid, phthalamic acid and n-phenyl phthalamic acid.

6. An artificial thread comprising a cellulosic material having opacity and/or low luster imparted thereto by the incorporation therein of an incompatible, finely divided substance comprising a salt of a polyvalent metal and n-phenyl-phthalamic acid.

7. An artificial thread comprising a cellulosic material having opacity and/or low luster imparted thereto by the incorporation therein of an incompatible, finely divided substance comprising a salt of a polyvalent metal and benzoyl-p-aminobenzoic acid.

8. An artificial thread comprising a cellulosic material having opacity and/or low luster imparted thereto by the incorporation therein of an incompatible, finely divided substance comprising a salt of a polyvalent metal and phthalic acid.

9. Artificial cellulosic films, filaments, and the like, containing an incompatible, finely divided opacifying and/or delustering agent comprising a highly insoluble and difficultly saponifiable, colorless salt of a metal and an aromatic acid having at least one cyclic nucleus highly deficient in hydrogen.

10. Artificial cellulosic films, filaments, and the like, containing an incompatible, finely divided opacifying and/or delustering agent comprising a highly insoluble and difficultly saponifiable salt of a polyvalent metal and an aromatic acid, said salt having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic medium.

11. An artificial thread comprising a cellulosic material having opacity and/or low luster imparted thereto by incorporation therein of an incompatible, finely divided substance comprising a highly insoluble and difficultly saponifiable salt of a polyvalent metal and an aromatic acid, said salt having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic medium of said structure.

12. The articles defined in claim 10 characterized in that said salt is colorless.

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CERTIFICATE OF CORRECTION.

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February 9, 1937.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 10, after the word "nitrocellulose" insert a comma; page 3, first column, line 67, claim 1, for "naphthol" read naphthoyl; 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 27th day of April, A. D. 1937.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.