

UNITED STATES PATENT OFFICE

2,069,807

CELLULOSIC SUBSTANCES AND METHOD
FOR PREPARING SAME

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14 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, nitro-cellulose, cellulose acetate 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 an heterocyclic compound 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. Another object of this invention is the production of a cellulosic structure containing as an opaquing and/or delusterizing agent, an heterocyclic compound containing one or more cyclic nitrogen atoms and one or more cyclic oxygen, sulfur, selenium or tellurium atoms. 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 low luster-inducing agent of the type hereinafter more fully described.

The opaquing and/or low luster-inducing agent contemplated by this invention is a mixed heterocyclic compound highly deficient in hydrogen and containing one or more cyclic nitrogen atoms and one or more cyclic oxygen, sulfur, selenium or tellurium atoms, whether the said hetero atoms are in the same or different heterocyclic nuclei and whether the said heterocyclic compounds are condensed or non-condensed, and preferably such mixed heterocyclic compounds containing at least four carbocyclic or heterocyclic nuclei.

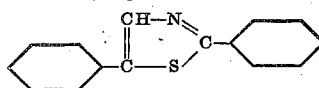
So far as the instant invention is concerned, each closed chain of carbon or hetero-atoms or combination of carbon and hetero-atoms will be considered a nucleus. Thus, benzene, naphthalene and carbazole have one, two and three nuclei respectively.

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.

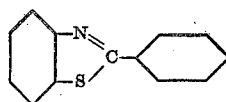
Highly effective delusterants function in particular by reason of their opacifying power which is a function of the difference in refractive index between the delusterant particle and the surrounding medium. Those in my preferred range differ from the index of the medium by at least 0.10 and the greater 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 mixed heterocyclic compounds coming within the scope of this invention, the following may be named:

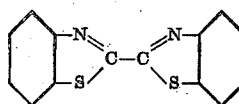
2,5-diphenyl-thiazole



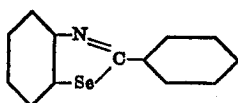
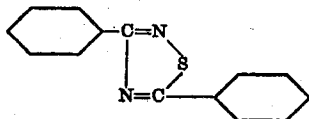
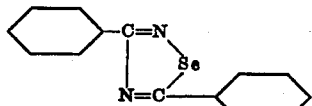
2-phenyl-benzothiazole



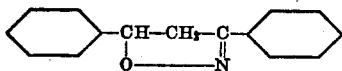
2,2'-bis-benzothiazolyl



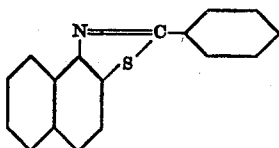
2-phenyl benzo-selenazole

3,5-diphenyl-thio-(alpha beta₁) diazole3,5-diphenyl-seleno-(alpha beta₁) diazole

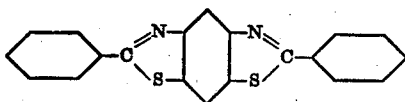
Alpha, gamma-diphenyl isoxazolin



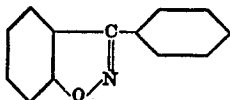
2-phenyl naphthothiazole



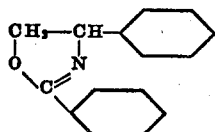
2, 2'-diphenyl benzo-bis-thiazole



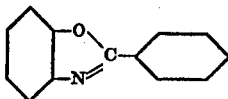
Gamma-phenyl-indoxazen



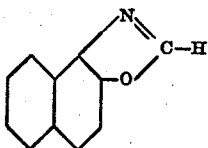
2, 4-diphenyl oxazole



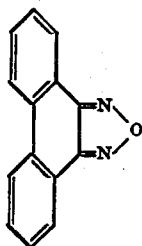
2-phenyl-benzoxazole



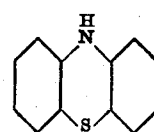
Naphthoxazole



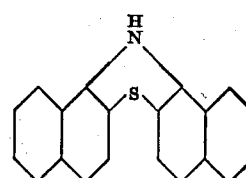
Phenanthrofurazane



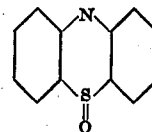
Thiodiphenyl amine



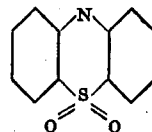
Thiodinaphthylamine



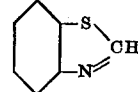
Diphenylamine sulfoxide



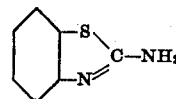
Diphenylamine sulfone



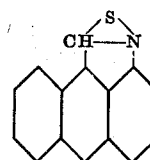
Benzothiazole



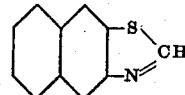
Amino benzothiazole



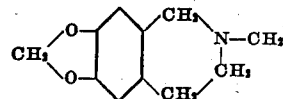
Anthraisothiazole



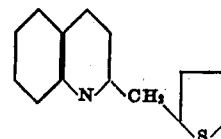
Naphthothiazole



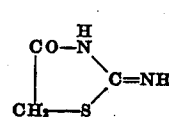
Hydrocotarnin



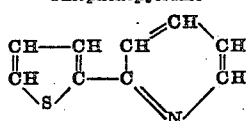
Alpha-thienylmethyl quinolin



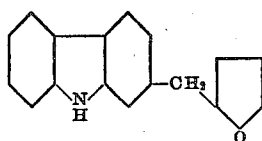
2-imino-4 thiazolidone



Thiophenopyridine



3-furfuryl carbazole



The scope of this invention is not intended to include heterocyclic compounds in which only nitrogen is present in a heterocyclic nucleus nor in which only one or more oxygen, sulfur, selenium or tellurium is present in a heterocyclic nucleus. In other words, this invention contemplates only those substances in which there is present, both a heterocyclic nitrogen atom and one or more heterocyclic oxygen, sulfur, selenium or tellurium atoms.

The compounds coming within the scope of this invention are

(1) Compounds containing —NH— or —N= and —O— , —S— , —SO— , $\text{—SO}_2\text{—}$, —Se— , or —Te— in the same nucleus such as thiodinaphthyl amine;

(2) Compounds containing —NH— or —N= and —O— , —S— , —SO— , $\text{—SO}_2\text{—}$, —Se— , or —Te— in the same condensed nucleus structure but not in the same ring, for example, hydrocotarnin; and

(3) Compounds containing —NH— or —N= , in one ring structure linked by carbon to rings containing —O— , —S— , —Se— , —Te— , —SO— , or $\text{—SO}_2\text{—}$, for example α -thienylmethyl quinolin.

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:

Phenylbenzothiazole, thiodiphenylamine, thiodinaphthylamine, 1-amino-3-methyl benzothiazole, 2-imino-4-thiazolidone, thiophenopyridine, 3-furfuryl carbazole.

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 0.10–20.0% 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 0.01–1.5% 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, lithopone, 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.—A sample of 2-phenyl benzothiazole (melting point 114°) is emulsified in the manner described in Example I in the co-pending application of W. W. Heckert, filed October 11, 1934 as Serial No. 747,933. The resulting emulsion is used in making up viscose in such proportions that the viscose contains 0.5% 2-phenyl benzothiazole and 7% cellulose. The viscose is spun into rayon or cast into films in the usual manner. The products are characterized by desirable opacity or low luster.

Example II.—Four hundred parts of diphenylamine sulfone (melting point 257°) are ground with 600 parts of water, 8 parts of sodium caseinate and 3,000 parts of pebbles in a pebble mill until all the particles have been reduced to a particle size below four microns in diameter. The resulting dispersion is used in making up viscose in such proportions that the viscose contains 7% cellulose and 0.4% diphenylamine sulfone. Viscose is spun into rayon or cast into sheets or other products in the usual manner. The products are characterized by a desirable opacity and low luster, much lower than that obtained with mineral oil as a delusterant.

Example III.—Four hundred parts of 2,2' bis-benzothiazolyl (melting point 306°) is ground with 8 parts of sodium caseinate and 3,000 parts of pebbles in a pebble mill until all the particles have been reduced to a particle size below four microns in diameter. The resulting dispersion is used in making up viscose in such proportions that the viscose contains 7% cellulose and 0.2% 2,2' bis-benzothiazolyl. The viscose is spun into rayon or cast into sheets or other products in the usual manner. The products are characterized by 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. 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 viscose process, it is obvious that the principles thereof are equally applicable to the cuprammonium cellulose, cellulose nitrate, and cellulose acetate processes.

In the case of cellulosic solutions of wholly organic solvents, it is only necessary that a suitable choice of mixed heterocyclic compound be made so that the solubility characteristics 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 in 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 thread. Thus, undelustered artificial thread 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 thread, 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. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, a finely divided white mixed heterocyclic compound highly deficient in hydrogen containing one or more cyclic nitrogen atoms and one or more cyclic atoms of the group consisting of oxygen, sulfur, selenium and tellurium.

2. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, a finely divided white mixed heterocyclic compound highly deficient in hydrogen containing one or more cyclic nitrogen atoms and one or more cyclic atoms of the group consisting of oxygen, sulfur, selenium and tellurium, said compound having a refractive index differing at least 0.1 from the refractive index of the cellulosic medium of the said cellulosic articles.

3. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, 0.1 to 20.0% of a finely divided white mixed heterocyclic compound highly deficient in hydrogen containing one or more cyclic nitrogen atoms and one or more cyclic atoms of the group consisting of oxygen, sulfur, selenium and tellurium, said compound having a refractive index differing at least 0.1 from the refractive index of the cellulosic medium of the said cellulosic articles.

4. Delustered artificial cellulosic articles containing, in a phase distinct from that of the

cellulosic material therein, a finely divided mixed heterocyclic compound taken from the group consisting of 2,5-diphenyl-thiazole, 2-phenyl-benzothiazole, 2,2'-bis-benzothiazolyl, 2-phenyl benzo-selenazole, 3,5-diphenyl-thio-(alpha beta₁) diazole, 3,5-diphenyl-seleno-(alpha beta₁) diazole, alpha,gamma-diphenyl isoxazolin, 2-phenyl naphthothiazole, 2,2'-diphenyl benzo-bis-thiazole, gamma-phenyl-indoxazen, 2,5-diphenyl oxazole, 2-phenyl-benzoxazole, naphthoxazole, phenanthrofurazane, thiodiphenyl amine, thiodinaphthylamine, diphenylamine sulfoxide, diphenylamine sulfone, benzothiazole, amino benzothiazole, anthraisothiazole, naphthothiazole, hydrocotarnin, alpha-thienylmethyl quinolin, 2-imino-4 thiazolidone, thiophenopyridine, 3-furfuryl carbazole.

5. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, 0.1 to 20.0% of a finely divided mixed heterocyclic compound taken from the group consisting of 2,5-diphenyl-thiazole, 2-phenyl-benzothiazole, 2,2'-bis-benzothiazolyl, 2-phenyl benzo-selenazole, 3,5-diphenyl-thio-(alpha beta₁) diazole, 3,5-diphenyl-seleno-(alpha beta₁) diazole, alpha,gamma-diphenyl isoxazolin, 2-phenyl naphthothiazole, 2,2'-diphenyl benzo-bis-thiazole, gamma-phenyl-indoxazen, 2,5-diphenyl oxazole, 2-phenyl-benzoxazole, naphthoxazole, phenanthrofurazane, thiodiphenyl amine, thiodinaphthylamine, diphenylamine sulfoxide, diphenylamine sulfone, benzothiazole, amino benzothiazole, anthraisothiazole, naphthothiazole, hydrocotarnin, alpha-thienylmethyl quinolin, 2-imino-4 thiazolidone, thiophenopyridine, 3-furfuryl carbazole.

6. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, a finely divided white mixed heterocyclic compound containing at least four carbocyclic or heterocyclic nuclei highly deficient in hydrogen, one or more cyclic nitrogen atoms and one or more cyclic atoms of the group consisting of oxygen, sulfur, selenium and tellurium, said compound having a refractive index differing at least 0.1 from the refractive index of the cellulosic medium of the said cellulosic articles.

7. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, 0.1 to 20.0% of phenylbenzothiazole in finely divided form.

8. Delustered artificial cellulosic articles containing, in a phase distinct from that of the cellulosic material therein, 0.1 to 20.0% of thiodinaphthylamine in finely divided form.

9. An artificial thread comprising regenerated cellulose having phenylbenzothiazole incorporated therein in finely divided form.

10. An artificial thread comprising regenerated cellulose having thiodinaphthylamine incorporated therein in finely divided form.

11. An artificial thread comprising regenerated cellulose containing, in a phase distinct from that of the cellulosic material therein, a white, finely divided mixed heterocyclic compound highly deficient in hydrogen containing one or more cyclic nitrogen atoms and one or more cyclic atoms of the group consisting of oxygen, sulfur, selenium and tellurium.

12. An artificial thread comprising regenerated cellulose containing, in a phase distinct from that of the cellulosic material therein, a white, finely divided mixed heterocyclic compound con-

taining at least four carbocyclic or heterocyclic nuclei highly deficient in hydrogen, one or more cyclic nitrogen atoms and one or more atoms of the group consisting of oxygen, sulfur, selenium and tellurium.

- 5 13. An artificial thread comprising regenerated cellulose containing in a phase distinct from that of the cellulosic material therein, a white, finely divided mixed heterocyclic compound containing
- 10 at least four carbocyclic or heterocyclic nuclei highly deficient in hydrogen, one or more cyclic nitrogen atoms and one or more cyclic atoms of the group consisting of oxygen, sulfur, selenium and tellurium, said compound having a refractive
- 15 index differing at least 0.1 from the refractive index of the cellulosic medium of said cellulosic structure.

14. An artificial thread comprising regenerated

cellulose and a mixed heterocyclic compound taken from the group consisting of 2,5-diphenylthiazole, 2-phenyl-benzothiazole, 2,2'-bis-benzothiazolyl, 2-phenyl benzo-selenazole, 3,5-diphenyl-thio-(alpha beta₁) diazole, 3,5-diphenyl-seleno-(alpha beta₁) diazole, alpha,gamma-diphenyl isoxazolin, 2-phenyl naphthothiazole, 2,2'-diphenyl benzo-bis-thiazole, gamma-phenyl-indoxazen, 2,5-diphenyl oxazole, 2-phenyl-benz-oxazole, naphthoxazole, phenanthrofurazane, 10 thioldiphenyl amine, thiodinaphthylamine, diphenylamine sulfoxide, diphenylamine sulfone, benzothiazole, amino benzothiazole, anthraiso-thiazole, naphthothiazole, hydrocotarnin, alpha-thienylmethyl quinolin, 2-imini-4 thiazolidone, 15 thiophenopyridine, 3-furfuryl carbazole.

WINFIELD WALTER HECKERT.