

UNITED STATES PATENT OFFICE

2,069,774

DELUSTERED CELLULOSIC STRUCTURE AND
METHOD FOR PREPARING SAME

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11 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 a sulfone or sulfoxide 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 explained.

The low luster-inducing and/or opaquing agent contemplated by this invention is an organic sulfone or sulfoxide having at least one and preferably two or more carboxylic or heterocyclic nuclei highly deficient in hydrogen, and their colorless derivatives such as those formed by substituting the following groups for hydrogen: —R, —O—R, —S—R, —Se—R, —Te—R, —NH—R, —CO—R, hydroxy alkyl or halogen, in which "R" may be an alkyl, aryl, alkaryl, aralkyl, or a heterocyclic group.

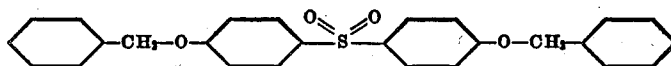
So far as the instant invention is concerned, each closed chain or carbon or hetero-atom or combination of carbon and hetero-atoms will be considered a nucleus. Thus, benzene, naphthalene and carbazole have one, two, and three nuclei respectively.

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.

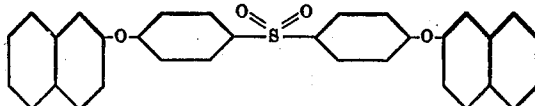
Highly effective delusterants function in particular by reason of their opacifying power which is a function of the difference in refractive index between the delusterant particle and the surrounding medium. Those in my preferred range differ from the index of the medium by at least 0.10 and the greater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

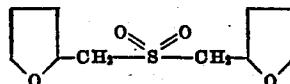
Dibenzyl ether of p,p' dihydroxy diphenyl sulfone



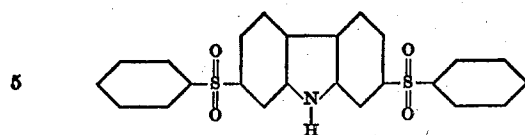
Dinaphthyl ether of diphenylol sulfone



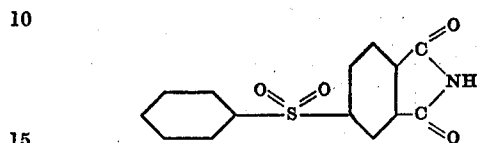
Difurfuryl sulfone



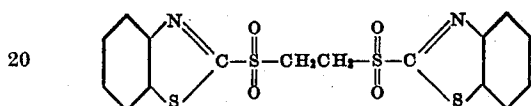
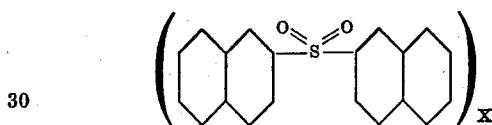
2,7 dibenzenesulfonyl carbazole



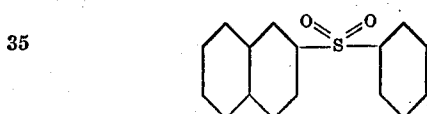
3-benzene sulfonyl phthalimide



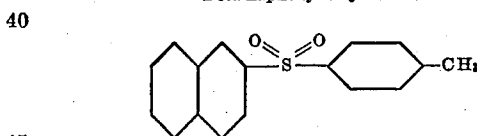
s-Dibenzthiazyl sulfonyl ethane

Dinaphthyl sulfone resin
Refractive index—1.70

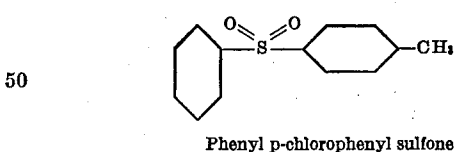
Alphanaphthyl phenyl sulfone



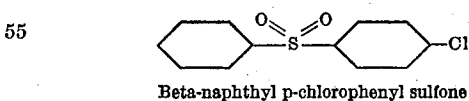
Beta-naphthyl tolyl sulfone



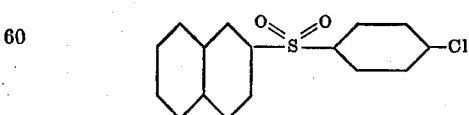
Phenyl p-tolyl sulfone



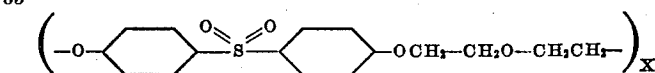
Phenyl p-chlorophenyl sulfone



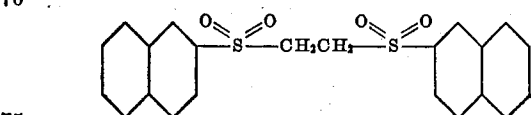
Beta-naphthyl p-chlorophenyl sulfone



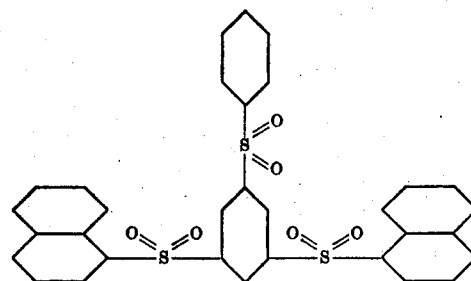
Diphenyl sulfone dichlorodiethyl ether resin



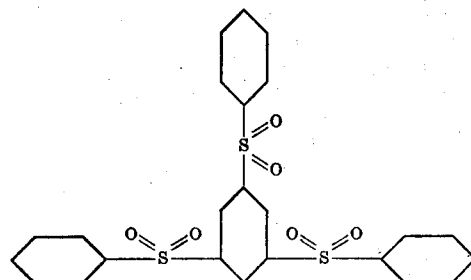
1,2 di-beta-naphthyl disulfonyl ethane



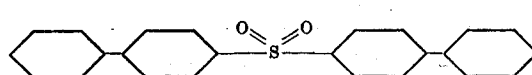
1,3,5 trinaphthyl trisulfonyl benzene



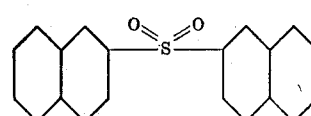
1,3,5 triphenyl trisulfonyl benzene



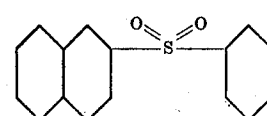
Di-biphenyl sulfone



Di-beta-naphthyl sulfone

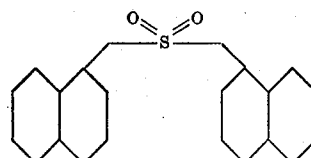


Beta-naphthyl phenyl sulfone

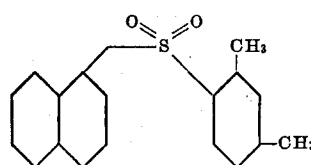


Di-alpha-naphthyl sulfone

Refractive index—1.66; 1.73; 1.79

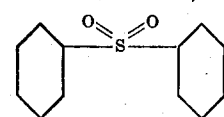


Naphthyl meta xylol sulfone



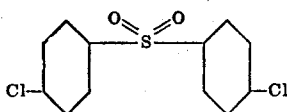
Diphenyl sulfone

Refractive index—1.69; 1.66

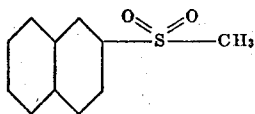


p-p' Dichlorodiphenyl sulfone

Refractive index—1.53; 1.75



Methyl-beta-naphthyl sulfone



As examples of sulfoxides may be mentioned the above sulfones in which the SO_2 group is replaced by an SO group.

Other specific sulfones which may be mentioned as included within the broad scope of this invention are:

Trimethylene trisulfone (ref. index—1.60; 1.66)

Hexamethyl trimethylene trisulfone, and

The sulfones and sulfoxides derived from spiro-bis-thiocyclobutane [see Rec. Trav. Chim. 52-499, (1933)]

The organic compounds contemplated as delusterants in accordance with the principles of this invention are embraced in the following formulae:



and



in which R or R_1 may be any organic group having a carbon atom which is directly linked to the sulfur atom.

The scope of this invention is not intended to include sulfonic acids or salts of sulfonic acids except as set forth by the above type formulae.

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

Methyl-beta-naphthyl sulfone,
Di-alpha-naphthyl sulfone,
1,3,5 Trinaphthalene-sulfonyl benzene,
1,3,5 Tribenzene-sulfonyl benzene,
1,2 Di-naphthyl ethylene disulfone,
Triphenylmethyle trisulfone,
Methyl dinaphtho sulfone.

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 beta-naphthyl phenyl sulfone (melting point 115°) is emulsified preferably in the manner described in the pending application of W. W. Heckert, filed October 11, 1934 as Serial No. 747,933, Example I. The resulting emulsion is used in making up viscose in such proportions that the final viscose contains 7% cellulose and 0.4% beta-naphthyl phenyl sulfone. The viscose is spun into rayon or cast into films in the usual manner. The products are characterized by a desirable opacity and low luster.

Example II.—Four hundred parts of di-alpha-naphthyl sulfone (melting point 188°) are ground with 600 parts of water, 8 parts of sodium caseinate, and 4000 parts of pebbles in a pebble mill until all the particles are reduced to a particle size of 4 microns or less in diameter. The resulting dispersion is used in making up viscose in such proportions that the viscose contains 7% cellulose and 0.4% di-alpha-naphthyl sulfone. The viscose is cast into films or spun into rayon. The products have a desirable opacity and low luster, much lower than that obtained with mineral oil, resembling that obtained with inorganic pigments.

Example III.—A sample of di-alpha-naphthyl sulfoxide (melting point 162°) is ground in the manner described in Example II. The resulting dispersion is used in making up viscose in such proportions that the viscose contains 7% cellulose and 0.1% di-alpha-naphthyl sulfoxide. The viscose is spun into rayon or cast into film in the usual manner. The resulting products have a desirable opacity and moderately low luster.

Example IV.—Four hundred parts of a diphenyl sulfone-dichlorodiethyl ether resin are ground in the manner described in Example I. The resulting pigment slurry is filtered (with the aid of a flocculating agent if necessary), dried and then dispersed in 1,600 parts of acetone by any suitable means such as violent agitation, grinding or passage through a colloid mill. The resulting acetone dispersion is used in making up a cellulose acetate spinning solution in such proportions that there is present one part of the resin for each ten parts of cellulose acetate. The cellulose acetate solution is spun into filaments or cast as a film in the usual manner. The products 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. In other words, the low luster-inducing agent may be applied to 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 sulfone or sulfoxide 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 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.

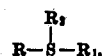
1. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising an organic compound embraced by the formula:



in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms.

2. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising an organic compound having two or more carbocyclic or heterocyclic nuclei highly

deficient in hydrogen and embraced by the formula;



and in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms.

3. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising an organic compound embraced by the formula;



in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms, said compound having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic base.

4. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising an organic compound having two or more carbocyclic or heterocyclic nuclei highly deficient in hydrogen and embraced by the formula;



and in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms, said compound having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic base.

5. Artificial cellulosic filaments and pellicles containing a cellulosic base and 0.1% to 20% of a finely divided, incompatible, substantially white, delustering and/or opaquing agent comprising an organic compound having two or more carbocyclic or heterocyclic nuclei highly deficient in hydrogen and embraced by the formula;



in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms.

6. Artificial cellulosic filaments and pellicles containing a cellulosic base and 0.1% to 20% of a finely divided, incompatible, substantially white, delustering and/or opaquing agent comprising an organic compound having two or more carbocyclic or heterocyclic nuclei highly deficient in hydrogen and embraced by the formula;



in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms, said compound having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic base.

7. Artificial cellulosic filaments and pellicles containing a cellulosic base and 0.1% to 20% of a finely divided, incompatible, substantially white, delustering and/or opaquing agent com-

prising an organic compound embraced by the formula;



5 in which R or R₁ may be any organic group having a carbon atom which is directly linked to the sulfur atom, and in which R₂ represents one or two oxygen atoms, said compound having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic base.

10 8. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising an organic compound taken from the group consisting of methyl-beta-naphthyl sulfone, di-alpha-naphthyl sulfone, 1,3,5 trinaph-

thalene-sulfonyl benzene, 1,3,5 tribenzene-sulfonyl benzene, 1,2 di-naphthyl ethylene disulfone, triphenylmethylen trisulfone and methyl dinaphtho sulfone.

9. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising methyl-beta-naphthyl sulfone. 5

10. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising di-alpha-naphthyl sulfone. 10

11. Artificial cellulosic filaments and pellicles containing a cellulosic base and a finely divided, incompatible delustering and/or opaquing agent comprising 1,3,5 triphenyl-trisulfonyl benzene. 15

EBENEZER EMMET REID.