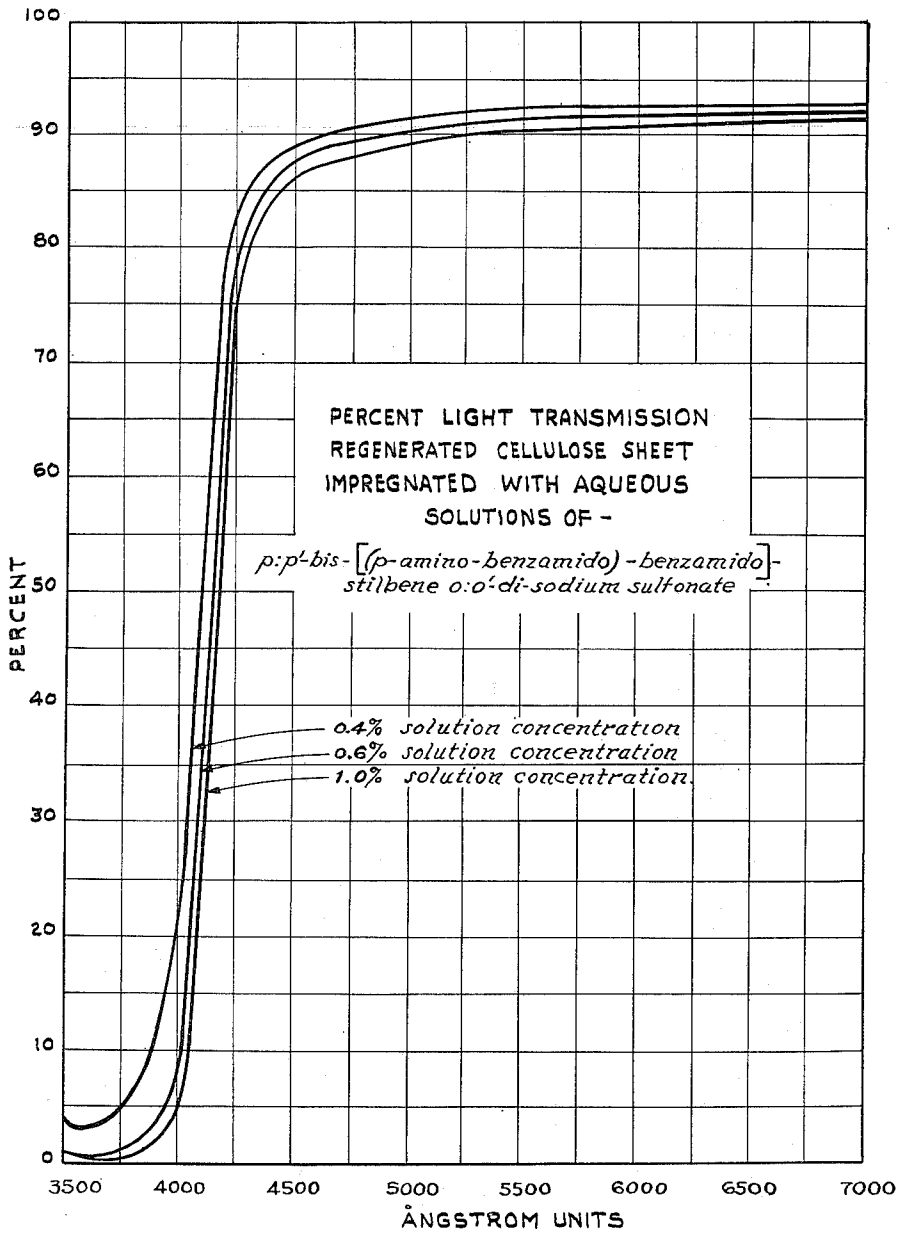
Dec. 5, 1944. B. VAN EVERY 2,364,112

MANUFACTURE

Filed Nov. 24, 1942



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Patented Dec. 5, 1944 2,364,112

UNITED STATES PATENT OFFICE

2,364,112

MANUFACTURE

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Application November 24, 1942, Serial No. 466,778

2 Claims. (Cl. 88—109)

This invention relates to transparent coverings and sheet wrapping materials capable of hindering or preventing rancidification of substances enclosed therein. More particularly it appertains to ultra-violet-light absorbing non-fibrous sheet, especially regenerated cellulose film and the like containing and/or associated with and/or joined with sulfonated bis-[(amino-benzamido-)benzamido] stilbene.

A sheet wrapping material which has come to the fore in recent years comprises a thin non-fibrous coherent self-sustaining cellulosic film. Typical procedures for manufacturing such film (foil, leaf, pellicle, sheet, skin, tissue, web) are described in U. S. A. Patents 1,548,864 (Brandenberger), 2,123,883 (Ellsworth) and 2,230,967 (Straughn). A considerable proportion of this sheet is coated, before use, to render it moisture-resistant. Representative coating compositions, and the application thereof, are set out in U. S. A. Patents 1,737,187 (Charch and Prindle), 1,826-697-8 (Charch and Craigue), 2,042,589 (Charch and Hershberger), 2,147,180 (Ubben), 2,159,151 (Hershberger), 2,169,366 (Meigs) and 2,201,747 (Staudt), and application Serial No. 430,885, filed February 14, 1942 (Mitchell).

In spite of the many desirable properties of both the plain and coated transparent regenerated cellulosic (having a structure similar to cellulose) film, its usefulness as a wrapper, for example, where the contents of the package are subjected to ultra-violet light, is severely circumscribed. Certain food products, particularly those containing oils and the like, for example, butter, when wrapped in such materials and stored in places lighted in ordinary ways, become rancid and frequently acquire an objectionable appearance, strong odor, undesirable taste, etc., in a fairly short time. Consequently, the sales value is correspondingly decreased. Some work designed to obviate this draw-back is described by Hunter in U. S. A. Patents Nos. 2,062,179, 2,129,131 and 2,129,132. See also U. S. A. Patents Nos. 2,038,114 and 2,043,860. Hunter proposed incorporating in such protective coverings selected light-absorbing dyes. These had certain draw-backs, including the conferring of considerable color or visible light absorbing capacity on the shielding material. Some of these dyes caused an uneven absorption of light in the visible spectrum (as viewed from the exterior of packages utilizing this wrapping material).

It appears that fat and oil-bearing foodstuffs are not appreciably affected, at least with regard to rancidity development during their normal storage or shelf-life, by light rays of any wave length within the bounds of the visible portion of the solar spectrum. Color in the wrapper is therefore unnecessary, and, if it could be eliminated without affecting the ultra-violet light-absorbing capacity, would appreciably widen the field of use. For example, colored sheet cannot be used with certain food products such as butter, which by law must be wrapped in material which does not enhance the yellow color (of the butter) or otherwise distort the appearance of the product so far as color is concerned.

The light rays which have been found to be particularly harmful, so far as rancidification is concerned, are found in the region of the near ultra-violet (near the visible spectrum), and even these harmful rays seem to be concentrated in certain narrow wave length bands. Marked photochemical action takes place in the above-mentioned foodstuffs and the like when they are exposed to light in the band 2900 A. to 3100 A. The same is true of the band from 3500 A. to 3700 A. This latter band is very close to the lower limit of the visible solar spectrum (4000 A.). Light in the lower band does not penetrate to an appreciable extent the type of glass commonly used for store windows, but this is not true of the 3500 A.–3700 A. Fairly large amounts of the light of this longer wave length are transmitted by window glass, bottle glass, etc. Since foodstuffs and commodities capable of rancidification are rarely exposed to direct sunlight, the light which normally falls on them being artificial or glass-filtered, it is apparent that the principal problem confronting the art is protection against light having a wave length in the range 3500 A. to 3700 A.

The primary object of this invention was to provide an inexpensive light filter capable of substantial absorption in the region of the near ultra-violet. Further objects were to provide a light filter having a substantially complete absorption of light having a wave length within the range 3500 A.–3700 A., and a substantially complete transmission of light having a wave length within the range 4000 A.–7000 A. (the visible spectrum); to provide a coherent covering film remaining stable over long periods of time, especially when subjected to solar light, heat, fats, oils, etc.; and to provide a flexible sheet wrapping material which is transparent, thin, moisture-proof, substantially colorless and substantially impermeable to ultra-violet light in the region of the wave length band of 3200 A.–4000 A. A still further object was to provide a sub-

stantially colorless sheet wrapping material having a regenerated cellulose base and being capable of inhibiting the development of rancidity of the type produced by photochemical action on the materials wrapped therein. Yet further objects were to provide colorless, ultra-violet light-absorbing wrappers for such materials as animal and vegetable oils and fats, oil-bearing foods and food products comprising the same such as salad oil, mayonnaise, butter, lard, potato chips, peanuts, and the like; to provide a colorless plain Cellophane capable of absorbing light of wave lengths falling within the range 3500 Å.–3700 Å.; and to provide a moisture-proofed non-fibrous, non-moistureproof cellulosic sheet wrapping material capable of transmitting at least 90% of the light in the visible spectrum, and absorbing at least 90% of light having wave lengths in the range 3500 Å.–3700 Å. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

It has now been found that dissolving, dispersing or otherwise finely distributing a bis-[(amino-benzamido-)benzamido-] di-sulfonated stilbene in or on a transparent self-sustaining covering film gives a sheet wrapping material which, without being colored, is capable of filtering out the ultra-violet light commonly causing rancidification of oil and fat-containing products.

The accompanying drawing comprises a graph showing curves plotted between the per cent of light absorbed and wave lengths in Ångstrom units for different concentrations of the stilbene derivative.

How the foregoing objects and related ends are accomplished will be apparent from the following exposition, in which are disclosed the principle and divers embodiments of the invention, including the best mode contemplated for carrying out the same. Parts are given by weight throughout the application unless otherwise specified.

Example I

Prepare a regenerated cellulose film, approximately 0.00088 of an inch thick, by extruding viscose into an acid coagulating and/or regenerating bath, desulfuring, bleaching and purifying in the customary manner, all, for example, as illustrated in U. S. A. Patent 1,548,864 (Brandenberger), passing the thus formed gel film through an aqueous bath at 180° F. (82° C.) having the composition:

	Per cent
p:p'-Bis-[p-(p-amino-benzamido-)benzamido-] stilbene-o-o'-di-sodium sulfonate	0.4
Glycerol	5.6
Water	94.0

removing the superficial liquid from the surface of the film by passage through squeeze rolls, and drying the film by passage over heated rolls in a warm dry atmosphere until approximately 6% moisture remains in the film.

The resultant film will contain approximately 1.2% of the light absorbent material and 16.5% of glycerol. It will be very flexible and will transmit better than 90% of the visible light above the wave length of 4500 Å. and less than 5% of the light of wave length between 3000 Å. and 3800 Å. The film will be highly transparent and practically colorless. There will be no deterioration in color or light transmission characteristics when the film is kept for long periods of time, for example, more than six months, at temperatures above 60° C., or when kept at ordinary temperatures for an equal period with exposure to direct sunlight for approximately 10% of the time. The curve for light transmission of such a film is indicated by the legend "0.4% concentration" in the drawing. The very sharp cut-off in light transmission at the edge of the visible spectrum is unique and very surprising.

Example II

Carry out the procedure of Example I, utilizing an impregnating bath comprising:

	Per cent
p:p'-Bis-[p-(p-amino-benzamido-)benzamido-] stilbene-o:o'-di-sodium sulfonate	1.0
Glycerol	5.6
Water	93.4

The light transmission characteristics for such film is indicated in the drawing by the curve bearing the legend "1.0% concentration." Films so produced will be very tough and flexible and well suited as a sheet wrapping material, particularly for the wrapping of butter, lard, peanut butter, crackers, etc. The resultant packages will be capable of being exposed in store windows for appreciable lengths of time without the contents being deleteriously affected.

Example III

Carry out the procedure of Example I, utilizing an impregnating bath comprising:

	Per cent
p:p'-Bis-[p-(p-amino-benzamido-)benzamido-] stilbene-o:o'-di-sodium sulfonate	0.6
Glycerol	5.6
Water	93.8

Films so produced will be very tough, flexible, highly suitable as sheet wrapping material, and have the light transmission characteristics indicated in the drawing by the curve bearing the legend "0.6% concentration."

Example IV

Soak a sheet of dried regenerated cellulose 0.00188 of an inch thick in an aqueous solution consisting of:

	Per cent
p:p'-Bis-[m-(m-amino-benzamido-)benzamido-] stilbene-o:o'-di-sodium sulfonate	2
Glycerol	10
Water	88

and maintained at 180° F. (82° C.) for 20 seconds. Remove the excess surface liquid and suspend the sheet freely in a warm atmosphere until it is dry. The resulting product will be practically colorless and will give excellent protection against the deleterious effects of sunlight when used as a wrapping material for oils and fats and foodstuffs containing oils and fats.

Example V

Coat a sheet of regenerated cellulose in the manner described in U. S. A. Patents Nos.

1,737,187, 1,826,696–8 with a composition consisting of:

	Per cent
p:p'-Bis - [p-(p - amino - benzamido-) benzamido-] stilbene-o:o'-di-sodium sulfonate	0.66
Cellulose nitrate (12.5% N.)	6.39
Dewaxed damar resin	1.58
Dibutyl phthalate	2.66
Paraffin wax (M. P. 61° C.)	.44
Ethyl acetate	52.34
Toluene	26.92
Ethyl alcohol	8.90
Acetone	0.11

When the solvents are evaporated, a lustrous clear film transmitting at least 90% of light within a wave length above 4500 Å. and less than 5% of light of wave length less than 3700 Å., will result.

Example VI

Coat regenerated cellulose film in the conventional manner with a composition comprising essentially:

	Per cent
p:p'-Bis-[m-(m-amino - benzamido -) benzamido-]stilbene-o:o'-di-sodium sulfonate	4.38
Cellulose nitrate (12.5% N)	5.84
Cellulose nitrate (11.5% N)	1.75
Dewaxed damar resin	1.44
Dibutyl phthalate	0.29
Dicyclohexyl phthalate	0.88
Ethyl acetate	50.34
Toluene	28.39
Ethanol	6.57
Acetone	0.12

A clear colorless film, giving excellent light protection especially in connection with the preservation of doughnuts will be obtained after evaporation of the solvent.

Example VII

Coat a regenerated cellulose web in the usual manner with a composition consisting of:

	Per cent
p:p'-Bis-[p-(m-amino - benzamido -) benzamido-]stilbene-o:o'-di-sodium sulfonate	1.80
Cellulose nitrate (11.5% N)	6.59
Dewaxed damar resin	1.02
Dibutyl phthalate	1.39
Cyclohexyl phthalate	3.89
Paraffin wax	0.33
Ethyl acetate	52.44
Toluene	27.37
Ethyl alcohol	5.17

The web obtained after evaporation of the solvent will be clear, transparent, colorless and moistureproof.

Example VIII

Pass a gel web of regenerated cellulose which has been cast from viscose, desulfured, bleached and washed in the conventional manner, as described in U. S. A. Patent No. 1,548,864 (Branderberger), through an aqueous bath containing:

	Per cent
Glycerol	4.3
Urea formaldehyde isobutanol resin (U. S. A. Patent 2,191,957)	0.75
Citric acid	0.08
p:p'-Bis - [p - (p-amino - benzamido-) benzamido -]stilbene-o:o'- di - sodium sulfonate	0.3

Maintain the web in contact with this solution for ten to twenty seconds, and thereafter remove the excess solution by means of squeeze rolls. Dry the sheet at a temperature of 60°–90° C. by passage through a drying chamber, followed by conventional drying rolls. Rehumidify the resulting sheet and coat it with a moistureproofing coating having the composition:

	Parts
Cellulose nitrate (12.5% N, 10 sec. viscosity)	6.70
Paraffin wax (M. P. 60° C.)	.15
Dibutyl phthalate	2.90
Dewaxed damar resin	1.50

The resulting transparent flexible odorless moistureproof sheet material will be very satisfactory as a wrapping in direct contact with products containing large amounts of moisture or water, such as butter, cheese and the like.

Example IX

Impregnate a gel web of regenerated cellulose which has been cast from viscose, desulfured, bleached and washed in the usual manner, with an aqueous bath containing:

	Per cent
Glycerol	4.3
Urea formaldehyde butanol resin (U. S. A. Patent 2,191,957)	0.75
Citric acid	0.08
p:p'- Bis - [p-(p-amino - benzamido -) benzamido -]stilbene-o:o'- di - sodium sulfonate	0.5

in the manner described in Example VIII. Squeeze and dry the sheet at a temperature of 60°–90° C. Coat the resultant sheet after rehumidification with the moisture-proofing coating of Example VIII. The resultant inexpensive, ultra-violet light absorbing, flexible, odorless, moistureproof sheet material will be very satisfactory as a wrapping in direct contact with products containing large amounts of moisture or water, such as butter and the like.

Example X

Pass a Cellophane web (regenerated from viscose) through an impregnating bath of the composition:

	Per cent
p:p'- Bis - [p-(p-amino - benzamido -) benzamido -]stilbene-o:o'- di - sodium sulfonate	0.4
Glycerol	5.3
Water	94.3

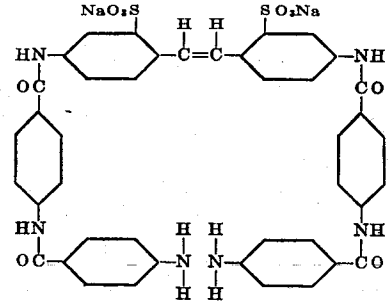
and dry the film in the usual manner. Pass the resultant web through a coating lacquer consisting of:

	Per cent
p:p'- Bis - [p-(p-amino - benzamido-) benzamido-]stilbene-o:o'- di-sodium sulfonate	0.66
Cellulose nitrate (12.5% N)	6.39
Dewaxed damar resin	1.58
Dibutyl phthalate	2.66
Paraffin wax (M. P. 61° C.)	.44
Ethyl acetate	52.34
Toluene	26.92
Ethyl alcohol	8.90
Acetone	0.11

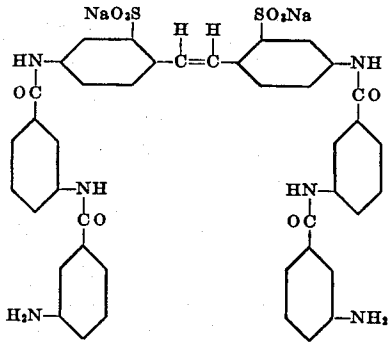
and remove the solvents in the manner customarily employed in moistureproofing Cellophane. A clear flexible sheet wrapping will result.

Two systems of nomenclature are available

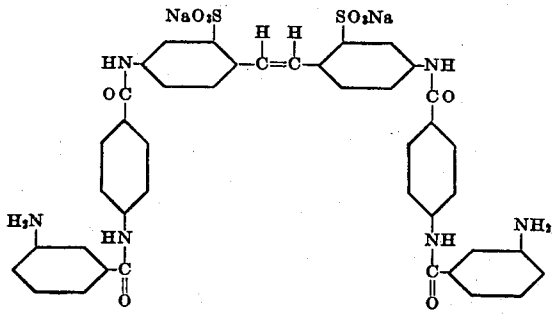
for use in connection with the light absorbing substances of this invention. The material used in Examples I, II, III, V, VIII and IX has the formula:



and may be called either p:p'-bis-[p-(p-amino-benzamido-)benzamido-]stilbene-o:o'-di-sodium sulfonate or the sodium salt of p:p'-di-amino-di-benzoyl-p:p'-di-amino - di-benzoyl-p:p'-di-amino-stilbene-di-sulfo acid. Similarly, the material used in Examples IV and VI, having the formula:



may also be called the sodium salt of m:m'-diamino-di-benzoyl-m:m'-di-amino-di-benzoyl-p:p'-di-amino-stilbene-di-sulfo acid, and the compound employed in Example VII, having the formula:



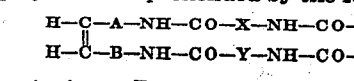
can be properly designated as the sodium salt of m:m'-di-amino-di-benzoyl-p:p'-di-amino-di-benzoyl-p:p'-di-amino-stilbene-di-sulfo acid.

The invention is not limited to the aforementioned specific compounds. One or more of the benzene rings in the disulfonated stilbene substituents may have their NH and CO connections in ortho, meta or para positions, and may have one or more of the hydrogen atoms replaced with halogen (chlorine, bromine, etc.), alkyl (methyl, ethyl, propyl, etc.), alkoxy (methoxy, ethoxy, etc.), etc. The sulfo group may be ortho or meta to the ethylene linkage in the stilbene residue.

The free sulfo acids, as well as the alkali metal salts (sodium, potassium, ammonium, etc.) are light absorptive materials. Both the mono- and di-alkali metal salts are satisfactory.

Mixtures comprising one or more of the light absorptive materials may be employed satisfactorily.

In any event, the light absorptive material employed is comprehended by the formula:



wherein A and B represent mono-sulfonated benzene residues and W, X, Y and Z represent benzene residues.

The concentration of the bis-[(amino-benzamido-)benzamido-]di-sulfonated stilbene per unit of area is important. So far no practical gain has been observed with less than 0.15 gram of the light absorbent per square meter of surface, and this amount may, therefore, be considered a practical minimum. In the preferred embodiments the light absorbent covering contains 0.5 to 1.0 gram of the light absorbent distributed uniformly over this unit area. No utility has been found for light absorbent in excess of 2.0 grams per square meter, so this is regarded as a desirable operating maximum. Obviously, later developments may show an advantage for the use of quantities outside the range 0.15 to 2.0.

The effect obtained with a given amount of the light absorbent is similar whether the material is incorporated (as by impregnation) in the sheet or covering material (Examples I, II, III and IV), distributed (uniformly) over one or both surfaces thereof (Examples V, VI and VII), or whether it occurs both in the body and in the surface coating (Examples VIII, IX and X). When employed in surface coatings, either a highly concentrated thin layer or a relatively less concentrated thick layer, may be employed. These light absorbents which are water soluble at least at elevated temperatures are easily incorporated in the water sensitive films.

For general application, that form of the invention which comprehends dispersion of the light absorbent in a coating composition on a base sheet or covering is considered the most useful, since it may be applied to a great variety of bases. Any type of coating composition may be used as a vehicle for the light absorbent, provided, of course, that the ingredients (solvents and solids) are compatible with, and/or dissolve or satisfactorily embody in sufficient amount, the light absorbent material. Transparency (to visible light) of the wrapper or covering is generally a desideratum, so the vehicle is ordinarily chosen so as not to interfere with the transparency of the base vehicle. It is appreciated, of course, that there will be rare instances where opacity may be desired for some special reason. All of the coating compositions commonly employed for coating bases of the type mentioned elsewhere herein, appear to be satisfactory.

Moistureproofing coatings are usually continuous unbroken layers containing essentially moistureproof material (material which does not dissolve more than an infinitesimal amount of, if any, water), for example, a waxy (wax-like) substance such as paraffin wax, and a cementing (binding, film-forming) material therefor, for example, cellulose nitrate. To improve the properties, inter alia, flexibility, of such coatings, plasticizing materials, for example, dibutyl phthalate, is generally incorporated therein. The base sheet as produced (whether it is coated or not) usually contains softening material, for example glycerol, and has, therefore, pliability adequate for a wrapping material.

To overcome any haziness which might result from some proportions and combinations of other components of the coating, transparentizing (blending, homogenizing) material, for example resins and gums such as damar and ester gum, is ordinarily included.

In the interest of brevity, for conventional details reference is made to the moistureproofing art, which includes the following U. S. A. patents:

1,826,696	2,094,771
1,962,338	2,096,122
1,972,869	2,098,534–542
1,989,681	2,100,377
1,990,080	2,122,418
1,997,583	2,122,433
1,997,857	2,137,636
2,022,490	2,144,383
2,030,962	2,147,628
2,042,638	2,147,629
2,061,374	2,159,007
2,064,292	2,177,645
2,065,792	2,192,314
2,077,396	2,193,831
2,077,399	2,205,210
2,077,400	2,205,428
2,079,379	2,209,965
2,079,395	2,213,252
2,085,816	2,216,812
2,087,013	2,234,565

Ordinarily, where the light absorbent is to be incorporated in the sheet or covering material itself, transparent, smooth, coherent, substantially non-porous non-moistureproof, nonfibrous, self-sustaining sheet, such as those composed of cellulosic (having the general structure of cellulose) material, for example regenerated cellulose, ethyl cellulose and cellulose acetate, albuminous material, for example gelatin and casein, and polyvinyl compounds, for example polyvinyl alcohols, polyvinyl esters and polyvinyl acetals and the like, are employed.

Water sensitive sheet obtained by coagulation or precipitation and/or regeneration from aqueous (or aqueous alkaline, for example metal hydroxide and the like) cellulosic or related dispersions (or solutions), for example viscose, cuprammonium and like regenerated cellulose, polyvinyl alcohol, low (lowly) substituted (less than one mol per glucose unit) cellulose ethers (U. S. A. Patent No. 2,123,880 to Ellsworth) such as glycol cellulose, cellulose glycolic acid, alkyl (methyl, ethyl, etc.) cellulose, and the like, are of especial interest.

The light absorbent may be incorporated in the self-sustaining films made from organic solvent soluble compounds, for example cellulose esters such as cellulose nitrate, cellulose acetate, cellulose aceto-butyrate, etc.; cellulose ethers such as ethyl cellulose, propyl cellulose, benzyl cellulose, methyl benzyl cellulose, etc., rubber, materials having some properties like rubber such as neoprene, rubber hydrohalides such as rubber hydrochloride, halogenated rubber such as chlorinated rubber, isomerized rubber, iratol (U. S. A. Patent No. 2,158,530 to Williams), resinous materials capable of forming coherent self-sustaining sheets, vinyl compounds capable of forming coherent self-sustaining films, hydrocarbon polymers, such as polythene, nylon, etc.

Where a semi-transparent or translucent wrapping is satisfactory the light absorbent may be incorporated in glassine paper. Where the only need is for a sheet material which will be impervious to ultra-violet light without regard to the transmission of visible light, it is possible to use ordinary paper, for example, thin tissue paper or heavier paper.

In some instances where the product to be protected can be satisfactorily so manipulated, it may be dipped into the solution or the dispersion of the light absorbent layer, whereby there is deposited thereon, by evaporation of the solvent from the adhering coating of the solution, a protective coating.

Ordinary moistureproofed Cellophane consists of a regenerated cellulose film 0.00088 of an inch thick, with a moistureproofing coating film 0.00005 of an inch thick on each side. The light absorbents of this invention function satisfactorily when incorporated in sheets thicker than either of these films.

Moistureproofness, moistureproofing and moistureproof materials and expressions are defined in U. S. A. Patent No. 2,147,180 (Ubben). In the interest of brevity the definitions are not repeated here. The terms and expressions related thereto and employed herein are used in accordance with such definitions.

Wherever the term "substantially complete absorption" is used, in connection with light and without further qualification, it signifies an absorption of at least 90%. By "transparent" is meant the transmission of at least 50% of the total available visible light. The word "colorless" is used to indicate the absence of appreciable selective absorption in the range of the visible spectrum (4000 A.–7000A.).

The sheet material obtained by following the specific examples, and equivalent procedures, may be used directly for the wrapping of foodstuffs and similar products to repress (restrain, avoid, curb, hinder, inhibit, obviate, prevent) undesirable changes therein. This is true whether the light-absorbent material is in any one of, or any combination of, the base sheet, the moisture-resistant coating, or between these two, for example in the anchoring layer for the moisture-resistant or moistureproof coating.

The new covering materials are used advantageously as a light-protection element in packages containing oils and fats, and foodstuffs containing or bearing oils, fats and the like, such as butter, peanut-butter, cashew-nut butter, lard, margarine, cheese, potato chips, doughnuts, vegetables, spices, mustards, etc. These coverings are also valuable for materials which may fade upon exposure to ultra-violet light, for example dyed fabrics. The films or sheets of this invention have good optical properties, and may be used for photographic filters, spectacles, and the like.

The invention offers numerous advantages heretofore unobtainable. New light filters capable of screening out virtually all of the ultra-violet light and transmitting a major proportion (over 90%) of the visible light applicable, are made available. This sheet wrapping material is capable of preserving oil-bearing commodities against rancidity development as induced by photochemical reaction of ultra-violet light, while still retaining transparency to visible light sufficient to render the commodities wrapped therein easily and attractively visible to the consumer. The covering materials fabricated in accordance with this invention remain stable over long periods of time, so that not only are the contents of the package protected against change in appearance and condition, but the wrapping itself remains unchanged in appearance and in

protective properties. The light absorbents utilized herein are substantially odorless and tasteless and are easily incorporated in the supporting films. They do not deteriorate with time or cause detrimental changes (deterioration, discoloration, etc.) in the support with aging under exposure to light over the range of the visible spectrum.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Substantially colorless, transparent regenerated cellulosic sheet wrapping material having associated therewith p:p'-bis-[p-(p-amino-benzamido-)benzamido-]stilbene-di-alkali metal sulfonate in amount sufficient to effect substantially complete absorption of light of the wave length of 3000 A. to 3800 A.

2. Substantially colorless, transparent regenerated cellulosic sheet wrapping material having associated therewith from 0.5 to 1.0 gram of p:p'-bis-[p-(p-amino-benzamido-)benzamido-]-stilbene-di-sodium sulfonate per square meter of the sheet wrapping material.

BLISS VAN EVERY.