

May 15, 1934.

E. E. RICHARDSON ET AL

1,958,714

PROTECTIVE OVERCOATING

Filed May 29, 1930

2 Sheets-Sheet 1

Fig. 1.

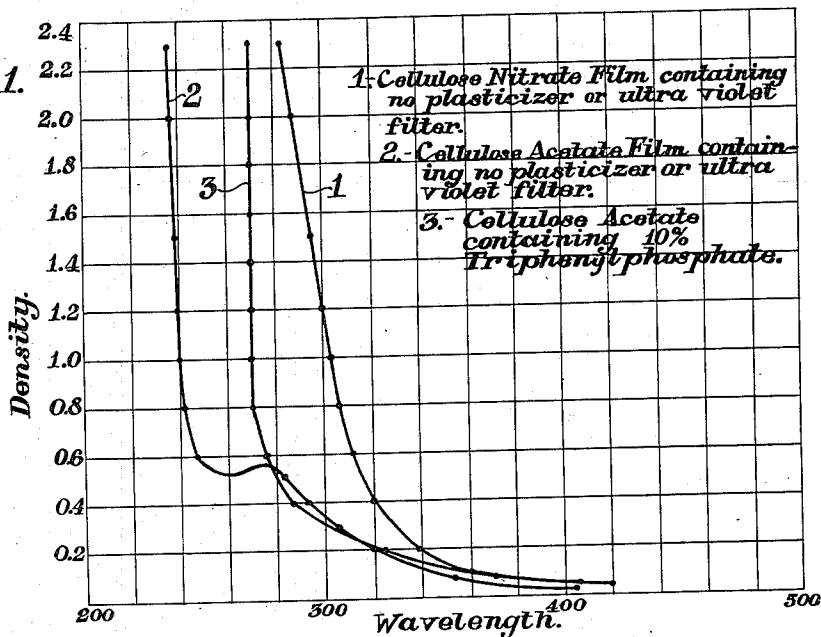
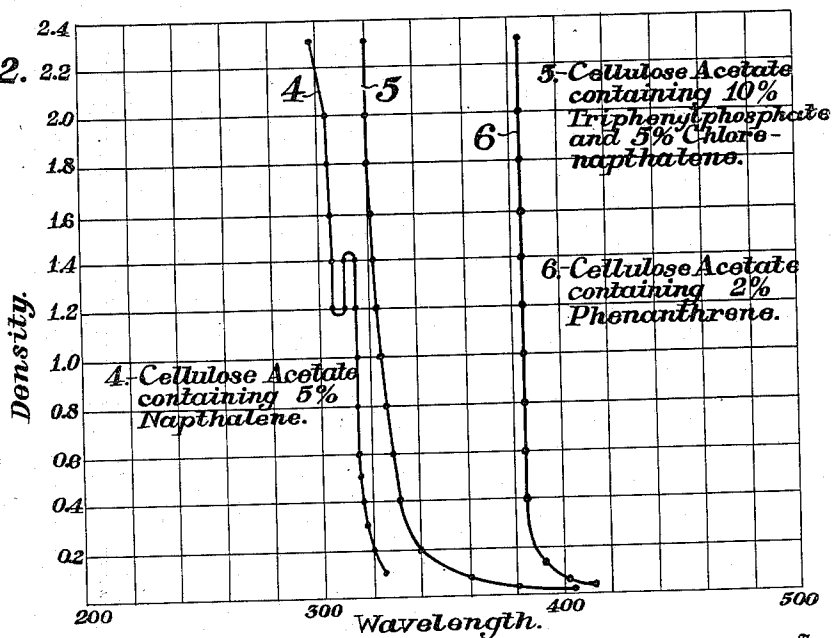


Fig. 2.



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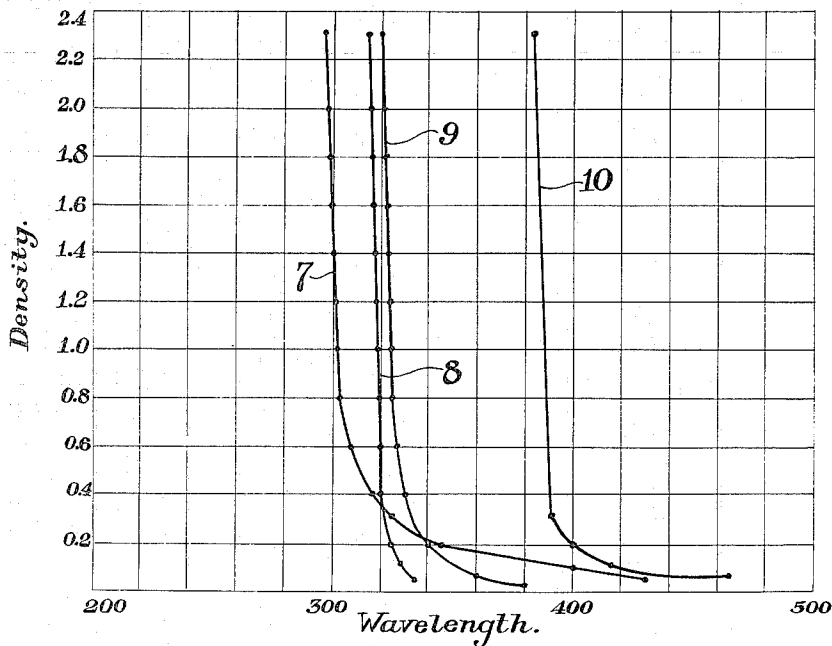
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2 Sheets-Sheet 2

Fig. 3.



- 7.-Cellulose Acetate containing 2%
Ortho Diphenyl Benzene.
8.-Cellulose Acetate containing 2%
Meta Diphenyl Benzene.
9.-Cellulose Acetate containing 2% Para Diphenyl
Benzene and 10% Triphenyl Phosphate.
10.-Cellulose Acetate containing 1% Anthracene.

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UNITED STATES PATENT OFFICE

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PROTECTIVE OVERCOATING

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Application May 29, 1930, Serial No. 457,508

12 Claims. (Cl. 91—68)

This invention relates to new types of protective coatings and particularly to cellulose acetate overcoatings which are applied over lacquer or other surfaces whereby the latter are protected from the short rays of light.

The cellulose nitrate lacquer industry has increased greatly in the past few years due, in part at least, to the ease with which this lacquer may be coated upon metallic and other surfaces, and to the rapidity with which these lacquer coatings dry. In the automotive industry particularly its use has released considerable of the materials which formerly were held in process and has, therefore, decreased markedly the expense incidental to the coating and finishing of the automobile. From the consumer's standpoint, however, cellulose nitrate lacquers have not appreciably increased the period of time during which his automobile or other lacquer finished product is kept from corrosion or in which it retains its initial glossy and fresh appearance,—it being a well known fact that cellulose nitrate loses its gloss with relatively great rapidity when exposed to the elements. The de-lustering and decomposition of cellulose nitrate surfaces, while to some extent due to inclement weather conditions, is primarily due to the ultra-violet rays from the sun which penetrates and decomposes the surface layer.

While the addition of pigments, gums, and plasticizers to the cellulose nitrate compositions aids to a slight extent in rendering the cellulose nitrate layer less affected by the ultra-violet light, the protection they afford is not by any means complete. With even a considerable amount of these constituents in the lacquer there is, nevertheless, upon the surface a good proportion of the cellulose nitrate directly exposed to the solar radiation. Moreover it has been found that the exposed cellulose nitrate under such conditions will be decomposed by the ultra-violet light incident to its surface. Furthermore, decomposition of the exposed cellulose nitrate will auto-catalyze the underlying cellulose nitrate particles which are in intimate contact with them. This auto-catalysis of the cellulose nitrate creeps through the whole surface with ever increasing velocity, with resultant decomposition which destroys much of the former lustre of the surface. To obviate these difficulties it has been suggested that a high gloss varnish or other transparent material be overcoated on the cellulose nitrate or other coating to inhibit its breakdown. While it has been previously suggested in the application of Paul C. Seel, Serial

No. 425,353, to overcoat nitrate lacquers with a clear lacquer containing cellulose acetate, we find that the protective effect of such acetate lacquer coatings may be materially improved, particularly from the standpoint of light protection, by preparing it in accordance with our invention.

An object of the present invention is to provide a filter for the absorption of the short light rays. Another object is to provide a cellulose acetate surface or overcoating which absorbs substantially all the ultra-violet light which has a deleterious effect upon the under-coating. Another object is to provide a cellulose acetate lacquer which having been applied in the usual manner absorbs many of the decomposing light rays. Other objects will hereinafter appear.

In our former U. S. application Serial Number 410,708, filed November 30, 1929, we have disclosed that cellulose acetate compositions which contain small percentages of naphthalene or chlorinated naphthalene such as alpha or beta chloronaphthalene have that property of inhibiting the passage of ultra-violet light. We have now found that the polycyclic hydrocarbons generally and their derivatives all have this unexpected property of inhibiting the passage of ultra-violet light. Under this general class of chemical compounds, naphthalene, chloronaphthalene, anthracene, phenanthrene, and ortho, meta and para-diphenylbenzene when present in cellulose acetate compositions all act as filters to prevent the passage of ultra-violet light.

In our research on these compounds we have found that in spite of the fact that triphenyl phosphate has the same number of phenyl groups as has phenanthrene or the diphenyl benzenes, nevertheless, triphenyl phosphate will not act as a suitable filter for the ultra-violet. Benzene alone also does not act as such a filter. We concluded, therefore, that the benzene rings should be fused as they are in phenanthrene or joined directly together as in the diphenyl benzenes if the compound is to act as an ultra-violet filter of sufficient opacity to protect such coatings and such proved to be the case, as all polycyclic hydrocarbons which we have been able to obtain and test have proven to be suitable ultra-violet filters. Also the following nitrogen-containing organic compounds have been found to have this quality of absorbing ultra-violet light to a greater or lesser degree, namely, diphenylguanidine, p-aminobenzoic acid, phthalimide, nitroanisole, nitrobenzol, quinaldine, benzyl benzoate, glycerol butyl phthalate, and B methoxyethyl phthalate

as set forth in separate applications of Staud, Richardson, Murray and Kocher, respectively.

Fig. 1 shows the absorption of light rays, unplasticized cellulose nitrate and acetate, and plasticized cellulose acetate.

Fig. 2 shows the effect on absorption by additions of phenanthrene and naphthalene.

Fig. 3 shows the effect on absorption by additions of diphenyl benzene and anthracene.

In the accompanying drawings will be found several spectro-photometric curves which very adequately depict the absorbing power of these compounds described herein as our invention. The spectro-photometer, as is well known, is a combination of a spectroscope and photometer into a single instrument which enables not only the wave length at which absorption takes place to be measured, but also the intensity of such absorption. In the accompanying drawings the abscissæ represent wave lengths in terms of millimicrons (1 millimicron equals 10 Angstrom units). On the ordinates are plotted the optical densities, the optical density being the logarithm of the reciprocal of the transmission. Expressed mathematically, if I_0 represents the incident light and I_1 the emergent light, then it follows that the transmission is a fraction of the total incident light represented as I_1/I_0 some having been absorbed by the material. The converse of the transmission would, of course, be opacity and be expressed by $1/T$ with T as the transmission. This, expressed in terms of the original symbols would be I_0/I_1 and the optical density is equal to the logarithm to the base ten of the opacity.

The accompanying table may be of assistance in reading the technical spectrophotometric terms and the attached drawings:

Transmission	Opacity	Density
1	1	0
.5	2	.3
.25	4	.6
.1	10	1
.01	100	2
.001	1000	3

In the spectro-photometric curve for cellulose nitrate shown in Figure 1, curve 1, it will be observed that absorption begins at a wave length of approximately 400 millimicrons, and that at 300 millimicrons over 90% of the light has been absorbed, while at 290 millimicrons nearly 99% of the light has been absorbed, and approximately 1% is transmitted.

From curve 2 of Figure 1 it will be clearly seen that the use of cellulose acetate alone in the overcoating for cellulose nitrate lacquers would be entirely ineffective in affording protection from ultra-violet light since the entire absorption curve of cellulose acetate lies in a shorter wave length than those of cellulose nitrate shown by curve 1, Figure 1, the main portion of the curve lying between 230 and 250 millimicrons. In this instance, of course, the cellulose acetate had no light filter present therein.

Cellulose acetate as an overcoating for cellulose nitrate, however, may be used as a vehicle for other materials, since in the terrestrial atmosphere no ultra-violet light of wave lengths 230 to 250 millimicrons occur. This is due to the presence of a sharp absorption band produced by what is thought to be due to ozone or other light filtering material in the earth's upper atmosphere which absorbs practically all the radiation between 220 and 288.5 millimicrons.

It is thus evident that the cellulose acetate itself will not decompose as rapidly as cellulose nitrate when subjected to the sun's rays, as the rays which decompose it do not reach the surface of the earth.

From a consideration of the above discussion, it will be realized that although cellulose acetate of itself does not decompose appreciably under the effect of ultra-violet light, it will not protect an under layer of cellulose nitrate over which it may be coated for the reason that it does not absorb those light rays which decompose the nitrate. By a review of the accompanying curves it will be seen that the ultra-violet absorption power of the cellulose acetate can be moved to the right of the cellulose nitrate curve, by the addition of the proper light filters thereto, thereby protecting the cellulose nitrate when such a cellulose acetate composition is overcoated thereon. In Figure 1, curve 3, is shown the effect of adding an ordinary plasticizer such as 10% triphenylphosphate to a cellulose acetate composition. While the original cellulose acetate curve has been shifted somewhat to the right by adding triphenylphosphate nevertheless it has not been shifted sufficiently to give to the acetate composition sufficient filtering quality to protect the cellulose nitrate. This phenyl containing compound, therefore, while it contains three phenyl groups does not have the required filtering qualities for removing the deleterious ultra-violet rays, as has been fully discussed hereinabove. The addition of 5% chloronaphthalene to the cellulose acetate film shown in Figure 2, curve 5, however, carries the acetate curve well to the right of the cellulose nitrate curve, thereby showing that such an overcoating of cellulose acetate will prevent all wave lengths of light less than 320 millimicrons from affecting any subcoatings upon which the cellulose acetate coating may be placed. In Figure 2, curve 4, is shown the effect of the addition of 5% naphthalene to cellulose acetate, here too it will be noted that the curve is sufficiently well to the right of the cellulose nitrate curve to afford good protection. The excellent absorption qualities of a cellulose acetate containing phenanthrene is well shown in Figure 2, curve 6. It will be noted here that a film of this nature containing even as low as 2% phenanthrene will absorb all the light rays shorter than 380 millimicrons. Figure 3 shows the effect of the ortho, meta and para-diphenyl benzenes when added in amounts of approximately 2% to the cellulose acetate. Curve 7 in this figure illustrates the filtering qualities of ortho-diphenyl benzene which absorbs approximately all the light shorter than 300 millimicrons, curve 8, which is the result of a test on cellulose acetate containing 2% of meta-diphenyl benzene shows a total absorption of approximately all light shorter than 300 millimicrons, while curve 9 for para-diphenyl benzene shows a somewhat better absorption of all light shorter than 320 millimicrons. Curve 10 for anthracene carries the absorption still further to the right substantially all short waves under 390 millimicrons being filtered out. As has been stated heretofore, while the addition of a larger quantity of these filter compounds to cellulose acetate will afford a somewhat greater absorption of the ultra-violet, this increase is generally not in proportion to the additional compound used. For example, in the case of chloronaphthalene, 1% will cut out all the short waves of approximately 310 millimicrons while 5% of chlorinated naphthalene only increases this absorption to waves of approximately 320

millimicrons. The addition of large quantities, therefore, of the filtering ingredient is not generally required or advantageous. It may also be stated that the meta and ortho diphenyl benzenes are readily soluble, at least up to 10%, in the usual solvents for cellulose acetate but that the para diphenyl benzene is not so readily soluble from .2 to .5 of one per cent being the usual amount which can be dissolved up in the usual solvents.

However as will be seen from the above, the addition of certain plasticizers such as triphenyl-phosphate assists in retaining the para diphenyl benzene in solution in amounts up to 2% or even more.

The amount of these filters required to afford protection to under coatings from ultra-violet radiations are of such small magnitude that no appreciable plasticizing effect would be observed. When present in the cellulose acetate layer in such amounts, therefore, they in no appreciable way affect the plasticity or the other physical qualities of the overcoating, but merely act as filters, preventing the passage therethru of the ultra-violet light. A larger amount of these substances in the cellulose acetate coating does not in any way lower the filtering effect but has a tendency to slightly increase the opacity of the film to the ultra-violet. In some instances the presence of 20, 30 to 50 per cent of the light filter, which is also suitable as a plasticizer, will eliminate the necessity of adding a separate plasticizer to the film. Whether or not the filter ingredients should be added in sufficient amounts to act also as plasticizers will in each case be determined by the type of filter used. Some of the filters are not particularly useful for this dual purpose because when they are present in a cellulose acetate film in amounts over and above that required to make the film opaque to the ultra-violet, the ingredients themselves objectionably tint or color the film. In any event the applications of Kocher, Serial Nos. 457,505 and 457,506 of even date cover this feature. If the filter then is to be employed in amounts only sufficient to give the desired filtering effect to the film, generally this requires from approximately $\frac{1}{4}$ -5%, and a second plasticizer such as triphenyl phosphate, alpha chloronaphthalene or the like many of which are well known in this art may be added in sufficient amounts to give the desired degree of plasticity.

We have found that it is not material what type of vehicle holds the filter as suitable varnishes, gums, shellacs, etc. for some purposes are equally as useful as incorporating the filter in a cellulose derivative. Nor should we be understood to restrict ourselves to cellulose acetate particularly as an overcoating cellulose derivative vehicle. There are numerous other such esters of cellulose, the mixed organic esters—cellulose aceto-propionate, cellulose aceto benzoate, etc., the mixed inorganic organic esters—cellulose nitro acetate, cellulose phospho acetate etc., or for that matter the other aliphatic organic esters of cellulose such as cellulose propionate, cellulose butyrates etc., many of which are useful in which to incorporate the filter for use as an overcoating. In selecting the vehicle it must, of course, be borne in mind that only those which are themselves not as rapidly decomposed, as the sub-coating which they are used to protect, are best suited.

Our novel filters may be prepared in the following manner altho any method of incorporating them in the particular vehicle which uniformly disperses the light filter thruout the ve-

hicle may generally be used. For example the cellulose acetate may be mixed with 3 to 10% of the light filter with or without the addition of say 50% of a plasticizer. This mixture may then be dissolved in a suitable solvent or solvent mixture such as one made up of 15% ethyl acetate, 50% acetone, 20% ethyl lactate and 15% denatured alcohol,—approximately one gallon of this solvent being required for 20 ounces of cellulose acetate. For the incorporation of some of the light filters other solvents or solvent mixtures may be more suitable, the above example being given merely to acquaint those skilled in the art with one manner of incorporating the filter. We are, therefore, not to be limited by the details or proportions of this example except as may be indicated by the appended claims.

It is evident from a study of the above disclosure that our invention covers the use of any type of filtering medium in a cellulose acetate overcoating which acts therein to render the same opaque to the passage of ultra-violet light, thereby protecting the sub-coating from deterioration due to this light. Cellulose acetate overcoatings containing sufficient amounts of the hereinabove indicated filters, or any suitable vehicle containing these filters will come within the scope of this invention, without sacrificing any of the advantages resulting therefrom. Also the term overcoating and the description of these overcoatings in connection with lacquers is to be understood broadly rather than specifically as it will be apparent that the value of our invention lies in the fact that by interposing between the cellulose nitrate layer and the source of the ultra-violet rays, a vehicle containing the ultra-violet light filter the nitrate underlayer will be protected from decomposition and deterioration. Thus, the cellulose acetate overcoating may consist of an already formed sheet containing the filter, which sheet is interposed between the cellulose nitrate sheet to be protected and the source of the ultra-violet light. Furthermore in the case of laminated glass, for instance, the cellulose derivative reinforcement interposed between the glass laminations may consist of a cellulose nitrate interlayer on either side of which is coated or otherwise imposed a layer or coating of a vehicle such as cellulose acetate with which has been incorporated an ultra-violet light filter. Thus, even tho the cellulose nitrate interlayer be covered on both sides with glass it is first covered with a vehicle containing an ultra-violet light filter so that the cellulose nitrate is protected from decomposition by the ultra-violet light which would otherwise penetrate the cellulose nitrate and decompose it. Thus, the term overcoating used in this specification and the appended claims is not to be confined to a mere lacquer top coat but is to be construed broadly as any shielding layer containing an ultra-violet filter for preventing decomposition of cellulose nitrate by ultra-violet light.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. An article of manufacture which has a closely adhering lacquer coating decomposable by sunlight, and a light-filtering overcoating comprising a cellulose organic derivative and a light-filtering substance, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the light-filtering substance, that it is absorbent of substantially all the rays of light shorter than 320

millimicrons, the light-filtering substance being present in the overcoating in an amount sufficient to substantially completely prevent decomposition of the lacquer coating.

2. An article of manufacture which has a closely adhering lacquer coating decomposable by sunlight, and a light-filtering overcoating comprising a cellulose mixed organic derivative and a light-filtering substance, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the light-filtering substance, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons, the light-filtering substance being present in the overcoating in an amount sufficient to substantially completely prevent decomposition of the lacquer coating.

3. An article of manufacture which has a closely adhering lacquer coating decomposable by sunlight, and an overcoating which comprises an organic derivative of cellulose and a polycyclic hydrocarbon, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the polycyclic hydrocarbon, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons, the light-filtering substance being present in the overcoating in an amount sufficient to substantially completely prevent decomposition of the lacquer coating.

4. An article of manufacture which has a closely adhering lacquer coating decomposable by sunlight, and an overcoating which comprises cellulose acetate and a polycyclic hydrocarbon, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the polycyclic hydrocarbon, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons, the light-filtering substance being present in the overcoating in an amount sufficient to substantially completely prevent decomposition of the lacquer coating.

5. An article of manufacture which has a closely adhering lacquer coating decomposable by sunlight, overcoated with a cellulose acetate composition containing a light-filtering substance, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the light-filtering substance, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons, the light-filtering substance being present in the overcoating in amount sufficient to substantially completely prevent decomposition of the lacquer coating.

6. An article of manufacture which has a closely adhering cellulose nitrate lacquer coating with an overcoating of a cellulose acetate composition containing a light-filtering substance, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the light-filtering substance, that it is absorbent of substantially all the rays

of light shorter than 320 millimicrons, the light-filtering substance being present in the overcoating in an amount sufficient to substantially completely prevent decomposition of the lacquer coating.

7. An article of manufacture having a closely adhering cellulose nitrate lacquer coating with an overcoating of cellulose acetate containing a polycyclic hydrocarbon, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the polycyclic hydrocarbon, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons, the light-filtering substance being present in the overcoating in an amount sufficient to substantially completely prevent decomposition of the lacquer coating.

8. An article of manufacture having a closely adhering cellulose nitrate lacquer coating with an overcoating of cellulose acetate containing from approximately ¼% to 5% of a polycyclic hydrocarbon, the overcoating being substantially transparent to visible light and having the characteristic, due to its content of the polycyclic hydrocarbon, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons.

9. An article of manufacture having a closely adhering coating decomposable by sunlight, and an overcoating comprising a cellulose organic derivative containing phenanthrene, the overcoating being substantially transparent to visible light and having the characteristic, due to its phenanthrene content, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons.

10. An article of manufacture having a closely adhering coating decomposable by sunlight, and an overcoating comprising cellulose acetate containing phenanthrene, the overcoating being substantially transparent to visible light and having the characteristic, due to its phenanthrene content, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons.

11. An article of manufacture having a closely adhering coating decomposable by sunlight, and a light-filtering overcoating comprising a cellulose organic derivative containing anthracene, the overcoating being substantially transparent to visible light and having the characteristic, due to its anthracene content, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons.

12. An article of manufacture having a closely adhering coating decomposable by sunlight, and a light-filtering overcoating comprising cellulose acetate containing anthracene, the overcoating being substantially transparent to visible light and having the characteristic, due to its anthracene content, that it is absorbent of substantially all the rays of light shorter than 320 millimicrons.

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