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ULTRA VIOLET LIGHT ABSORBING COMPOSITIONS HAVING
A SUSPENSION OF SUBMICRON PARTICLES
Filed Oct. 26, 1962

3,298,959

FIG. 1

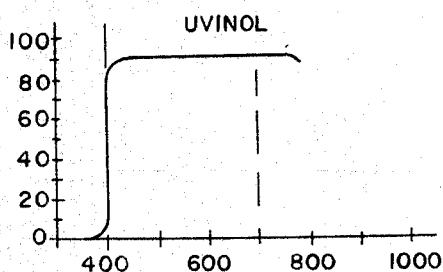


FIG. 4

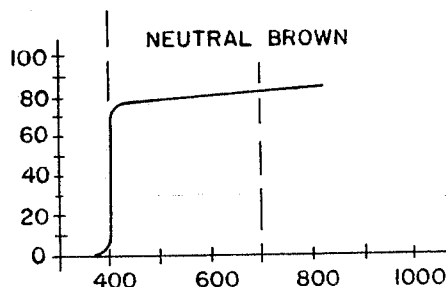


FIG. 2

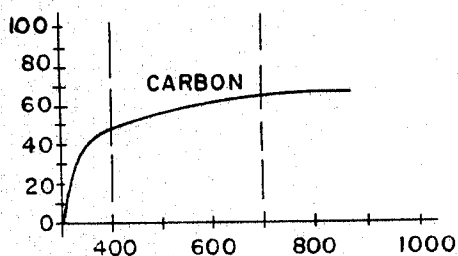


FIG. 5

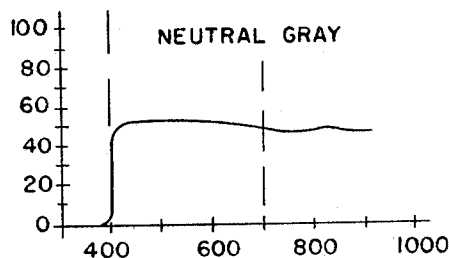


FIG. 3

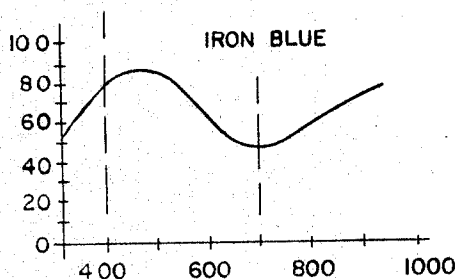
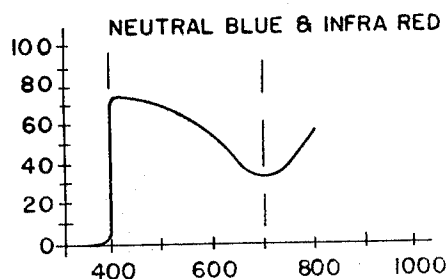


FIG. 6



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1

3,298,959

ULTRA VIOLET LIGHT ABSORBING COMPOSITIONS HAVING A SUSPENSION OF SUBMICRON PARTICLES

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9 Claims. (Cl. 252-300)

This invention relates to selective light absorbing film forming compositions and particularly compositions for coating large area surfaces with light filtering materials having the property of absorbing ultraviolet light almost completely, and modifying visible and infrared light, and is a continuation in part of an application filed in the name of Alvin M. Marks and Mortimer M. Marks on Oct. 7, 1958, Ser. No. 765,781, now abandoned.

Where it is desired to coat large area surfaces to produce a uniform thin adherent film having suitable light absorbing properties, the method and apparatus set forth in U.S. Patent No. 2,721,809 issued Oct. 25, 1955, has been found most effective. This method and apparatus is hereinafter referred to as the "flow coat technique."

In practicing the "flow coat technique," a temporary trough is attached to the bottom of a vertically disposed window or large glass area to be coated. The flow coat film forming composition which is contained in a tank under pressure, is forced through a clearing filter, a solvent-resisting nozzle, a hand-controlled valve and out of an applicator wand. The window is masked around the edges. One vertical edge of the window, such as the left edge, is wetted by drawing the applicator wand downwards or upwards and allowing the liquid coming therefrom to flow downwardly along this edge. The window is then completely coated by slowly moving the applicator wand across the top of the window from left to right at a controlled speed and permitting the liquid composition to flow downward and across the window in a preferably unbroken coating. When the applicator wand reaches the upper right hand corner of the window, it is moved down the right edge to wet this edge.

This operation may be performed manually or by machine. The excess liquid flows into the lower trough, which is preferably made of stiff cardboard or aluminum foil. The excess liquid may then be sucked into another storage tank, for subsequent reuse after the addition of a small amount of solvent (about 5%) and refiltration. After the fluid composition applied to the window has thoroughly drained and dried, a hard, thin transparent uniform film remains on the window.

A fluid plastic solution employed for the above operation must have certain properties and meet extremely rigid specifications in order to be suitable for use in performing the process, and producing the desired result.

Accordingly, it is an object of the present invention to provide transparent compositions for the uniform flow coating of surfaces, characterized in that, when drying, they form films having the following properties:

(1) Transparency to visible light: selective absorption in very thin films ranging from 0.1 to 1 mil thickness, of visible light producing a neutral or colored film, absorption of ultraviolet light and partial absorption of infrared light;

(2) Transmission of visible light without appreciable scatter;

(3) Drying while producing a perfectly plane surface;

(4) Adherence to glass both when dry and when subjected to high humidity;

(5) Prolonged resistance to the variable effects of light, heat and cold;

2

(6) Sufficiently hard to bear repeated cleaning.

Another object of the present invention is to provide a fluid coating composition which has the following properties:

(1) Flow characteristics such that the film dries to a smooth surface without striae or "orange peel";

(2) A drying rate low enough to enable flow downward for long distances (10 to 15 feet), and to enable excess liquid to drain off, but fast enough to cause rapid hardening within 15 to 30 minutes;

(3) A suitable viscosity range such that ready flow occurs, not too heavy, nor too thin, since viscosity controls final film thickness.

(4) Operable with a wide range of ordinary atmospheric conditions of temperature and humidity (from 10° to 40° C. and 20% to 90% relative humidity) and must dry to a uniform film under these conditions;

(5) Components including the light filtering materials which either go into solution, or form a transparent suspension, substantially free from the scattering of transmitted light.

The film forming compositions of the present invention when dried are very transparent to visible light, but absorb nearly all of the ultraviolet light in the 300-395 mμ region. Ultraviolet light below 300 mμ is absorbed by most glasses. When the light filtering coating of this invention is applied upon glass, it is not required that the coating composition absorb ultraviolet light below 300 mμ. This is of particular advantage when the light filtering compositions are utilized for flow coating glass windows.

One of the film forming compositions of this invention which is of particular utility for flow coating applications, dries to form an adherent, uniform, neutral grey color coating which absorbs all visible colors approximately equally. Thus this composition does not distort color. The composition absorbs ultraviolet light completely in the near ultraviolet region from 300-395 mμ, and partially absorbs invisible deep blue light in the region from 395-405 mμ, as well as also absorbing a predetermined proportion of visible and infrared light. Such a filter film provides maximum protection from the destructive effects of the sun's rays, while providing maximum visibility without color distortion, and without light scatter.

Another composition of this invention dries to form a thin uniform film that absorbs all ultraviolet light up to 400 mμ and highly transmits visible and infrared light from 400 to 1000 mμ.

Still another composition totally absorbs all ultraviolet light up to 400 mμ and accomplishes this in a film thickness of the order of 0.0001" to 0.0010". The light absorbing compositions of this invention are highly stable, thin and economical, and may be readily applied by known coating techniques to a variety of surfaces including such as are employed in the graphic arts for the protection of pigments, dyes and photographic images.

Still another composition of this invention has the above light absorption characteristics, and further has a predetermined absorption of infrared light in the region between 700-1200 mμ.

Reflections from surfaces coated by this composition are substantially reduced since the second surface reflection component is strongly absorbed.

A feature of this invention is the use of a suspension of conducting or semi-conducting particles in selected size ranges, chosen particularly to reduce or eliminate the scatter of visible light. We have discovered that such suspensions form a basis for a neutral density screen which strongly absorbs ultraviolet light, and partially transmits visible and infrared light in a predeterminable manner. Such suspensions are highly stable and efficient

absorbing media having high utility for the absorption of selected spectral ranges, and provide excellent visibility without appreciable light scatter.

The light filtering compositions of this invention may be employed in a lamination between glass or plastics, thus providing laminated panels having the light absorbing characteristics above described. These compositions are capable of certain variations which may be controlled in the manufacture to provide panels meeting a variety of specifications required in the construction industry. Such panels are of great utility for use as windows.

A preferred technique for applying these compositions to surfaces employs spin coating for the manufacture of such laminated light filtration panels, as disclosed in Patent No. 2,632,725 dated Mar. 24, 1953, to Alvin M. Marks and Mortimer Marks, and entitled Method of Laminating Lenses.

While the coating and lamination techniques described above are preferred under certain conditions, other conventional techniques may also be employed for the coating of surfaces. For example, in the graphic arts, conventional roller coating technique or even spray coating of surfaces may be employed using the compositions of this invention.

Examples of compositions according to the invention are hereinafter described with the help of the attached graphs of percent transmission versus wavelength given by way of examples, in which:

FIGURE 1 is a graph for an ultraviolet absorber used in the invention.

FIGURE 2 is a graph of a carbon black suspension having a particle size averaging 9 $m\mu$ in transparent film.

FIGURE 3 is a graph for a Prussian Blue suspension in a transparent film.

FIGURES 4, 5 and 6, are curves representing combinations of individual components illustrated in FIGURES 1 through 3, which result in light absorbing compositions having unique properties.

FIGURE 4 shows the transmittance vs. wavelength curve for an ultraviolet absorbing light filtering composition which transmits a predetermined amount of visible and infrared light, and which comprises a combination of Curves 1 and 2, there being a usually minor proportion of the absorber shown in FIGURE 1. When a substantial amount of material having the characteristics shown in FIGURE 2 is employed, the color is a neutral brown tint.

FIGURE 5 shows essentially the same curve as FIGURE 4, but with a minor proportion of the component whose characteristic is shown in FIGURE 3, which results in the unique composition which has a neutral grey color, and which totally absorbs ultraviolet light and transmits a predetermined amount of visible and infrared light.

FIGURE 6 shows essentially the same curve as FIGURE 5 but modified, in that a larger proportion of the blue infrared absorbing component shown in FIGURE 3 is employed: such that a neutral blue tint is obtained with a substantial increase in the infrared absorption.

The characteristics shown in FIGURES 4, 5 and 6, with the degree of control afforded by those compositions, provide a range of shades and tints, together with protective characteristics in the ultraviolet and infrared which have great utility as previously described.

We have discovered that suspensions of the type described above, have certain unique properties where particle size is less than 50 $m\mu$, and preferably in the size range averaging about 10 $m\mu$, down to 1 $m\mu$. For example, particles of 9 $m\mu$ average size do not show appreciable scatter. They are well below the size ($\frac{1}{4}$ micron) where resonance or dipole absorption occurs, and they thus act to absorb radiation due to the physical blocking of their cross sectional area in the visible and infrared. However, we have discovered that such particles possess, in the ultraviolet region (about 300-400

$m\mu$) an electro-magnetic cross section greater than their actual physical cross section. It is theorized that considerable resonance absorption occurs due to higher harmonics of the incident light; this being especially pronounced for wave lengths of 410 $m\mu$ and less. The transmittance characteristic of a suspension of such particles is shown in FIGURE 2.

We have further discovered that such absorption characteristics can be achieved with very small quantities of these suspensions, because particles having such small radii, produce a very large number of particles per unit area of a given film thickness, of extremely large total cross sectional area. This total physical cross sectional area is inversely proportional to the radius of particles in a given film thickness and in direct proportion to the percent absorbed by weight of film.

We have found that the characteristic curve shown in FIGURE 2 has considerable, but not complete absorption in the ultraviolet; and that complete absorption of the ultraviolet light may be achieved by the addition of relatively small quantities of ultraviolet absorbers.

A preferred ultraviolet absorber is 2,2' dihydroxy-4,4' dimethoxy benzophenone, which may be dissolved to a maximum proportion of approximately 10% in most clear film forming compositions; requiring, in such case, a film thickness of about 0.7 mil to obtain the characteristic curve shown in FIGURE 1.

Other ultraviolet absorbers known in the art, which have similar characteristics to that shown in FIGURE 1, may be used alternately, without departure from the scope of this invention.

An increase in the concentration of the ultraviolet absorber, such as above noted, has resulted in the film becoming supersaturated with the ultraviolet absorber, with subsequent crystallization and clouding of the film.

Reduction of both film thickness and ultraviolet absorber concentration is desired to maintain film clarity to facilitate coating operations, and to provide an economical composition. The conventional ultraviolet absorbing materials are relatively very expensive compared to the light absorbing suspensions of the type herein described.

The combinations of light absorbers shown in FIGURES 4, 5 and 6 produce the illustrated light transmission versus wavelength characteristics, which have negligible light scatter in a thin transparent film capable of transmitting an image without loss of contrast. The total absorption of ultraviolet is thus achieved in a relatively thin stable clear film containing only 1 to 10% of ultraviolet absorber, which depends for its major absorption characteristic upon a relatively inexpensive particle suspension in the film.

Suspension materials of this type have been used as pigments for opaque coatings, where the problem of light image transmission with negligible light scatter was not encountered. The combinations of absorbers and film formers herein disclosed which have unique optical and physical characteristics, are thus new and novel.

Clear base compositions.—An example of a clear base lacquer composition for use in the present invention is as follows:

(a) 30% $\frac{1}{4}$ sec. nitrocellulose solution	Formula A
Dry $\frac{1}{4}$ sec. nitrocellulose	30.00
Ethyl alcohol	12.9
Sub total	42.9
Ethyl alcohol	3.3
Ethyl acetate	8.0
Amyl acetate	16.0
Toluol	29.8
Total	100.0

Various other grades of nitrocellulose may be substituted.

5

- (b) An alkyd resin in proportions such as coconut oil acid 57%, phthalic anhydride 43%, to 60% solids, in xylol.
- (c) Styrene-acrylonitrile copolymer, 50% solids in xylol.
- (a), (b) and (c) are mixed producing a homogeneous solution, for example, as set forth below.

EXAMPLE 1

Prepare the following solvent:

Solvent composition B—	
Butyl acetate	433
Xylene	450
Cellosolve acetate	117
Total	1000

The components of the Solvent "B" have the following properties:

Solvent Mixture "B"	Percent By Weight	P ₂₀ mm. Hg Vapor Pressure at 20° C.	Boiling Point ° C.	Evaporation Rate Designation
Butyl Acetate	43	7.8	126.6	Intermediate.
Xylene	45	4.9	144.4	Intermediate.
Cellosolve Acetate	12	1.2	156.4	Slow.

Other solvents, known in the art, of the "Intermediate" and "Slow" evaporation rate designation, such as are listed below, may be substituted for the solvents "B" in approximately the proportion 5–25% slow solvents, and the balance mixtures of intermediate solvents. The listing is in the order of evaporation rate, the next below being slower.

Evaporation rate of various liquids

"Intermediate":

N-propyl alcohol	Xylene.
1-nitropropane	Amyl alcohol.
Methyl-n-butyl ketone	Methyl-n-amyl ketone.
Isobutyl alcohol	Cellosolve.
Amyl acetate	Methyl "Cellosolve" acetate.
n-butyl ether	Cyclohexanone.
Xylene	Ethyl lactate.
	Dichloropentane.
	"Cellosolve" acetate.
	Diisobutyl ketone.

"Slow"

A preferred clear base solution is as follows:

Component	Solution	Solids	Percent Solids
(a)	140	42	23
(b)	100	60	33
(c)	160	80	44
Solvent B	600		
Total	1,000	182	100

Solids=18.2%.

The clear base of this example possesses necessary characteristics set forth above for the practice of the flow coat process with light filtering compositions of this invention.

EXAMPLE 2

The composition of Example 1 may be modified within certain limits, as hereinafter given:

Let x =percent of component (a).
 Let y =percent of component (c).

Then the following additional examples of clear bases are given. In this example, total solids may comprise 18 to 30% in solvent composition B:

- (a) $40 > x > 10$
 (b) $100 - (x + y)$
 (c) $24 < y < 80$

6

EXAMPLE 3

Examples of clear base compositions which have good adhesion to surfaces of gelatin and cellulose acetate; and which may be used after incorporating the light absorbing compositions herein described, are as follows:

- (a) $10 < x < 40$
 (b) 0
 (c) $90 > y > 60$

These compositions may be used, for example, for coating photographs and prints containing pigments or dyes to protect them from fading.

EXAMPLE 4

An adhesive clear base coating for glass surfaces which may thereafter be laminated, is as follows:

Solvent C:	
Butyl acetate	20
Toluol	40
n propanol	40
	100

The solvent C may be replaced by other solvents well known in the art.

Dissolve the following in solvent C to 12–22% solids:

Polyvinyl butyral	100– x .
Plasticizer	$15 < x < 40$.

Plasticizers such as dibutyl phthalate or others well known in the art may be substituted. Also a $\frac{1}{4}$ to 2% of adhesive silicate compound such as silicic acid may be employed.

Light absorbers may be incorporated in this composition, herein disclosed, to form a film having a thickness of .0005" to .0035" on glass sheets. The coating and lamination of this film between two plates of glass, may be performed according to well known processes, as noted above.

The absorbing agents 1, 2 and 3 hereinafter described are added to the clear base, for example, as shown in Examples 5–8 inclusive, as to thus obtain light transmittance characteristics shown in the figures.

The light absorbers.—As light absorbing agents, certain insoluble pigments are preferred which are available as dispersions in nitrocellulose and which are suitable for forming clear transparent films with the clear base compositions disclosed herein; as well as certain soluble absorbers which are capable of forming a clear solid solution with the dried film. For example, Absorber No. 1 described hereinafter, is particularly efficacious for the absorption of ultraviolet light only. The soluble and suspended insoluble absorbers are combined as hereinafter specified, to produce the absorption characteristics herein described.

Absorber No. 1.—FIGURE 1 shows the percentage of transmission versus various wavelengths for a preferred ultraviolet absorber composition, comprising a substituted benzophenone: 2,2 dihydroxy-4,4'- dimethoxy-benzophenone. Other known soluble transparent ultraviolet absorbers, having absorption characteristics similar to that shown in FIGURE 1, may be substituted without departing from the scope of this invention.

Absorber No. 2.—Absorber No. 2 comprises a certain suspension, in which the particles have a maximum diameter of less than 50 μ , and an average particle size of about 9 μ . When the particle size is thus limited, light is transmitted with substantially no scatter and the film remains clear even in bright sunlight. Larger size particles produce objectionable light scatter, and cannot be used in the production of transparent films.

FIGURE 2 shows the percentage transmission versus wavelength for a preferred carbon suspension in nitrocellulose, which is available as solid lacquer chips. This ab-

sorber has a gradually increasing transmittance in the visible spectrum from 410 $m\mu$ –700 $m\mu$, and the transmittance shows a further gradual increase for infrared light from 700–1000 $m\mu$. The gradually increasing transmittance from 410 $m\mu$ to 1,000 $m\mu$, results in a neutral brown shade. There is a partial absorption in the 395–410 $m\mu$ region. There is increasingly strong absorption as 300 $m\mu$ is approached.

Absorber No. 2 may be made up as follows:

Material	Solution	Solids	Percent Solids
Absorber of black lacquer chips, comprising:			
Carbon (9 $m\mu$ average size).....	166	22	13.3
Nitrocellulose.....		144	86.7
Butyl acetate.....	834		
Total.....	1,000	166	100.0

Percent solids=16.6.

Percent C in total solution=2.2.

The above composition is by way of illustration in which the percent C may vary from 5–50%, and the balance nitrocellulose.

In lieu of a carbon suspension, there may be used a suspension of conductors such as metals, such as aluminum, gold, etc. or semi-conductors such as silicon, tellurium, provided the particles have a dimension that is smaller than that which produces a noticeable light scattering effect, and are approximately of an equivalent size and concentration as to give the required absorption characteristic, as given in connection with Absorber No. 2.

With conducting or semi-conducting particles, the absorption maxima is obtained when resonance is established, and the free electrons within the particle oscillate with the frequency of incident radiation, dissipating the radiant energy by resistive or ohmic loss. Resonance occurs when the particle diameter approaches $\frac{1}{2}$ wavelength, however, excessive scatter of visible light also occurs in this size range.

Elongated rod or platelike particles, can absorb electromagnetic radiation from a cross sectional area of space of some 10–100 times their physical cross section.

By known means, a mixture of different sizes of particles may be separated into specified size ranges, which show absorption in selected wavelength ranges. Special absorption and transmission characteristics may be obtained by selected particle size ranges, as a result of preferred absorption at certain wavelengths. We have found, however, that only small particles in the range 1–50 $m\mu$, particularly near 10 $m\mu$, will transmit light in all directions without appreciable scattered light. In a film medium of index of refraction $N=1.5$, the wavelength (blue) 450 $m\mu$ in air, corresponds to 300 $m\mu$ in the film medium; for which $\lambda/2=150$ $m\mu$.

MATHEMATICAL THEORY

Table of symbols

a =Film thickness
 A_p =Cross section of the particle= πr^2
 $C=fg$ ="coverage" efficiency (1=100%)
 D ="Optical density" of the film= $\log_{10}(100/T)$
 δ =Density of particle
 f =Electromagnetic cross section coefficient
 g =Particle agglomeration factor
 K =Actual exponential absorption factor
 K_0 =Ideal exponential absorption factor
 m =Mass of the particle= $4/3\pi r^3\delta$
 M =Mass of absorber/unit area= $ap\delta$
 N =Number of particles/unit area
 p =Proportion of absorber in film by weight
 r =Radius of particle, assumed spherical
 T =Transmittance

T' =Percent transmittance

V =Volume of the particle

x ="Coverage," or proportion of area obscured; or, total cross-sectional area of particles/unit area.

Assumptions

(1) There is no overlapping of particles.

(2) Particles absorb exactly in proportion to their cross-sectional area relative to total cross section. In this case, the electromagnetic cross section factor $f=1$.

(3) There is no agglomeration of particles.

$$N=M/m=ap\delta/(4/3)\pi r^3\delta \quad (1)$$

$$x=A_p N \quad (2)$$

$$x=\pi r^2 \cdot ap/(4/3)\pi r^3 \quad (3)$$

$$x=(3/4)p(a/r) \quad (4)$$

$$T'=100(1-x) \quad (5)$$

$$x=(100-T')/100 \quad (6)$$

Equating 4 and 6 and solving for p :

$$p=4/3(r/a)[(100-T')/100] \quad (7)$$

Assuming the following values for particle radius r , and film thickness, a :

$$r=10 \text{ } m\mu=10^{-6} \text{ cm.}$$

$$a=.0004''=10^{-3} \text{ cm.}$$

Substituting these values in Equation 7 we obtain:

$$p=1.33 \times 10^{-3}(100-T')/100 \quad (8)$$

The proportion of absorbing particles by weight is larger, when measured experimentally, due to the random overlapping and aggregation of particles.

The simple form of Equations 7 and 8 apply only to thin sections Δa and small changes in transmittance ΔT made in accordance with the assumptions.

For small changes in transmittance ΔT , and for small changes in a thickness Δa , for light which has traversed a thickness " a " having a transmittance T , Equation 7 may be modified to the following differential form:

$$-\Delta T=(3/4)(p/r)T\Delta a \quad (9)$$

Integrating 9:

$$T=e^{-K_0 a} \quad (10)$$

Where the ideal exponential absorption factor K_0 is given by:

$$K_0=(3/4)(p/r) \quad (11)$$

Since the section Δa is thin and ΔT small, overlapping of particles is not a factor in Equation 10.

Resonance effects, which may increase or decrease the absorption as a function of (λ/r) may be taken into account by an electromagnetic cross section factor, f .

Agglomeration of particles, which decreases the absorption, may be taken into account by an agglomeration factor, g .

The factors, f and g , are combined to given the "coverage efficiency," C :

$$C=fg \quad (12)$$

The coverage efficiency, C modifies the ideal exponential absorption factor to provide the actual exponential absorption factor, K , as follows:

$$K=CK_0=C(3/4)(p/r) \quad (13)$$

Hence, from 12 and 13:

$$K=(3/4)fg p/r$$

Equation 10 may now be written to include the coverage efficiency:

$$T=e^{-(3/4)C(p/r)a}=e^{-Ka} \quad (15)$$

To express 15 in terms of optical density:

$$D=\log_{10}(1/T)=[\log_{10} e](3/4)(Cp/r)a \quad (16)$$

$$D=0.325 (Cp/r)a \quad (17)$$

$$Cp=3.08 (r/a)D=3(r/a)D \quad (18)$$

Coverage efficiency—measurements

Example: Given a film with 63% transmittance:

$D=0.2$ "optical density"

Substituting into 18 for D, and using the same values of "r" and "a," which were used in 8:

$Cp=3(10^{-6}/10^{-3})0.2=6\times10^{-4}$ (19)

Data concerning the upper and lower limits of percent carbon in a neutral shade coating according to this invention is hereinafter given in Example No. 7. In this example the upper and lower limits of percent carbon may be computed by noting that Absorber No. 2 produces substantially all of the absorption at about 550 mμ:

Lower Limit: 400 parts Absorber No. 2 at 2.2% C=8.8 pts. C.

Upper Limit: 1600 parts Absorber No. 2 at 2.2% C=35.2 pts. C.

These are added to 18.2% clear base solution of Example No. 1.

Let C₁=lower limit of carbon conc.

Clear base solids:

$(10,000-400) 0.182=1750$ pts.

Absorber No. 2 solids:

$400\times0.166= 67$ pts.

Total Solids 1817

$C_1=(8.8/1817)100=0.5\%$

Let C₂=upper limit of carbon conc.

Clear base solids:

$(10,000-1,600) 0.182=1530$

Absorber No. 2 solids:

$1600\times0.166= 266$

1796

$C_2=(35.2/1796) 100=2.0\%$

Hence

$2\times10^{-2}>p>5\times10^{-3}$ (20)

From 19 and 20, the percent coverage efficiency, percent C, may be computed:

$3\%<\text{percent C}<12\%$ (21)

It is probable that the electromagnetic absorption coefficient, f, is much less than 1 in the visible range, with $(r/\lambda)<(1/30)$. Hence, the small coverage efficiency factor is probably only partially due to agglomeration. Hence the limits for p will vary from about .01 to 10%.

The following table summarizes some of the above results:

Percent Trans., Percent T	Optical Density, D	Coverage, X	Proportion Of Absorbing Particles By Weight, Percent	
			p	Cp
0.1	3.00	0.999	0.130	0.090
63.0	0.20	0.370	0.044	0.060
90.0	0.05	0.100	0.013	0.015
Formula Number		(6)	(8)	(17)

We have found that particles averaging less than about λ/30, where λ=450 mμ in air, do not scatter visible light appreciably.

From FIGURE 2 and the preceding mathematical discussion, it is found that such particles absorb the longer wavelengths in the visible and infrared region without appreciable light scatter by a factor of 10 to 50 times less than their total physical cross section. However, these same particles show an absorption of ultraviolet light at 300 mμ, of about ten times the physical cross section of the particles, which may be attributed to electron reso-

nance within the particles to the electromagnetic radiation field. Hence an enhanced absorption cross section for such particles, at least for the short ultraviolet wavelengths, appears to occur below 375 mμ.

As shown in FIGURE 2, for the carbon suspension (Absorber No. 2) the light transmission increases uniformly beyond 450 mμ, the transmitted light thus being a brown color. The carbon suspension absorbs considerable ultraviolet and dark blue light in range 395-405. A small amount of carbon suspension, in combination with a soluble ultraviolet absorber, acts as an effective ultraviolet absorber without adding noticeably to the color of the transmitted light, and without introducing appreciable scatter. Consequently when Absorbers No. 1 and No. 2 are used in combination, a smaller proportion of ultraviolet Absorber No. 1 is required for the complete elimination of ultraviolet light. The soluble ultraviolet absorbers are generally quite expensive while the carbon suspension or equivalent is comparatively inexpensive. This combination for the absorption of ultraviolet light and near blue light is more efficient and economical than Absorber No. 1 used alone, and this combination is not subject to crystallization in thin films. Thus a light absorbing composition with new and unexpected properties is provided.

Absorber No. 3—iron blue (Prussian blue).—The characteristics of Absorber No. 3 are shown in FIGURE 3. Prussian blue forms submicron transparent crystals which have less tendency to scatter than suspensions of opaque particles. Nevertheless, scatter is minimized by utilization of these particles in the same size range utilized for Absorber No. 2. To obtain the neutral shade shown in FIGURE 5, just enough of Absorber No. 3 is utilized to balance out the brown color.

A typical composition is:

Material		Solids
Pigment (Prussian Blue)	30.0	30.0
N/C 30-35% (Dry Base)	18.0	18.0
Dibutyl Phthalate	6.4	6.4
Ethyl Alcohol	27.6	
Ethyl Acetate	18.0	
Total	100.0	54.4

Percent Solids=54.4%.
Percent Pigment in total=30%.

The above composition is by way of illustration. The pigment may vary from 5-50% and the balance comprising N/C and plasticizer. The parts by weight may vary from 10-60%.

Use of absorbers in coating compositions.—There is a critical range of compositions for the Absorbers 1, 2 and 3 in the clear base carrier film.

For best results, Absorber No. 1 appears to exist in solid solution in the carrier film. It has been found that with Absorber No. 1 in excess of 10% of solids, crystallization occurs in the coating, which reduces efficiency and causes light scatter. Under 10%, this does not occur. If the concentration of Absorber No. 1 is under 5% of the solids, however, insufficient ultraviolet absorption occurs in a thin film, as noted below.

However, using Absorber No. 1 and Absorber No. 2 in combination, the percent of Absorber No. 1 in the solids can be reduced to as little as 1 to 2% based on solids, when the white light transmission is 25-75%. Not only does this reduce the danger of crystallization, but a much more economical mixture results.

For the denser shades of FIGURES 4, 5 and 6, for a transmittance of 20% or less, the percentage of Absorber No. 1 may be drastically reduced or eliminated completely.

Flow coat compositions.—After air drying on a glass plate, held vertically, the film thickness commonly obtained with the flow coat process, may be, for example, 0.0005" on 6" length of flow. Thicknesses from .0003"

to .0010" may be obtained on a 6 to 10 ft. of flow from top to bottom, after thorough drying.

A 6" length may be chosen as a convenient standard for film thickness measurement, which may be made optically (after calibration with a micrometer) by measurement of percentage transmission with a white light photometer.

For example, with a solids content of 20% and Absorber No. 1 present to the extent of 7% in these solids, a film thickness of .00055" was measured on 6" flow at 20° C. The following percentage transmittance versus wavelength was obtained.

M μ :	Percentage
370 -----	0.0
380 -----	0.2
390 -----	7.5
400 -----	41.0
410 -----	73.0

Transparent panel laminate compositions.—To provide transparent coated or laminated panels, the proportions given in the above examples may be used with the lamination solution given in Example 4. The transmittance characteristics of FIGURES 1-6 inclusive may be obtained. The characteristics of FIGURES 4, 5 and 6 are particularly desirable for light control in the ultraviolet, visible and infrared.

The compositions of this invention may be utilized in the manufacture of transparent panel laminates having the known characteristics of welding glass, and meeting the standard optical transmittance specifications therefor. Such specifications call for a lower transmittance in the infrared than in the visible region, extending out to about 3 microns. To achieve these results, the herein described compositions, which result in the characteristics in FIGURES 5 and 6, may be further modified to exclude the far infrared by the incorporation of a transparent silver foil such as is available commercially, or, preferably a transparent silver film plated onto one or both inner surfaces of the glass panels used in the laminate. Alternatively gold or other transparent metallic films may be utilized, or multilayer dichroic films having the required blocking characteristics of the far infrared may be employed. In the case of the transparent silver film, a transmittance of the order of 1 to 20% may be utilized according to the shade number of the welding glass. For example, with shade No. 10, a 12% transparent silver foil may be employed. A composition similar to that of No. 6 having a suitable optical density, is included in a lamination solution such as that given in Example No. 4 and laminated as above described, to obtain the shade of welding glass required.

EXAMPLE 5

To obtain the percentage transmission versus wavelength characteristics of FIGURE 1 (with ultraviolet absorption only)

140 to 180 parts of Absorber No. 1= x .

(10,000- x) of clear base solution, such as given in Examples 1-4 inclusive.

EXAMPLE 6

A neutral brown shade such as is shown in FIGURE 4 and which strongly absorbs ultraviolet light and partially absorbs infrared light may be produced as follows:

Absorber No. 1 (ultraviolet absorber) -----	0-140
Absorber No. 2 (carbon suspension) -----	1600-400
x =totals -----	1600-540

10,000- x clear base solution, such as given in Examples 1-4 inclusive.

EXAMPLE 7

A neutral shade coating which strongly absorbs ultraviolet light and partially absorbs blue light, and transmits visible light from 420-700 m μ approximately equally, and which partially absorbs infrared light, may be produced utilizing the following composition:

Absorber No. 1 (ultraviolet absorber) -----	0-140
Absorber No. 2 (carbon suspension) -----	1600-400
Absorber No. 3 (Prussian blue) -----	60-15
	1600-555

x =(total absorbers including solvents and suspended colloids) and 10,000- x of clear base solution, such as given in Examples 1-4 inclusive.

A white light transmission about 65% is obtained after flowing vertically on glass 6" below the start and drying.

EXAMPLE 8

A neutral blue coating which absorbs ultraviolet light and transmits a blue visible shade, and which absorbs infrared light more strongly in accordance with the spectrum shown in FIGURE 6, may be produced by the following composition:

Absorber No. 1 -----	140
Absorber No. 2 -----	170
Absorber No. 3 -----	40
	350
Clear base solution such as given in Examples 1-4 inclusive -----	9650
	10,000

White light transmission: 67%.

In this composition Absorber No. 1 may be varied from 35-140 parts, Absorber No. 2 from 100-500 parts, and Absorber No. 3 from 25 to 125 parts.

Products of this invention may be used as self-supporting films, coatings on various supporting materials or as laminates, with film thickness of .0002" to .0020", and approximately still provide the absorption characteristics given above.

With a film thickness of .00055" and 2% of a carbon particle suspension there is no need for an ultraviolet absorber. Such a film will substantially absorb all ultraviolet light. However, the resultant film will be very dark. By employing 0.1 to 0.5% carbon and 3 to 7% of an ultraviolet absorber, a film having a high visible light transmittance can be achieved which will totally extinguish ultraviolet light.

The percentage of absorber will be inversely proportional to the thickness of the film. Film thickness can, therefore, be decreased providing that Absorber No. 1 does not increase beyond 10%. For very thin films the ultraviolet absorption must be mainly that obtained by the carbon suspension, which can be present up to about 20% of total solids.

Coating compositions having light filtration properties in accordance with this invention, produce transparent or translucent films which are colorless, neutral shade or colored, and which absorb ultraviolet light almost totally, and absorb visible and infrared light in predetermined amounts. Transparent films having no appreciable light scatter, may be produced with these transmittance properties, or translucent films may be purposely produced by adding a known light scattering agent. Such film coatings are useful for screening the harmful rays of visible light, particularly those rays which have the greatest chemical action, which produce destructive effects on numerous products in the food and drug industry, and deterioration of the dyes and colors of fabrics and various graphic art products. Excessive ultraviolet and infrared light produce fatiguing effects upon human beings.

Coatings of this invention are particularly suitable for application by the flow coat process for the covering of large window areas with smooth, adherent, protective films. Coatings according to this invention, having the herein described optical properties, may also be applied to glass or plastic transparent panels, and then fabricated to form a laminated panel. Coatings, according to this invention have also found use in protective tubular shields for fluorescent lights, where they screen out the emitted harmful ultraviolet light, and the excess blue color of the light.

Certain modifications within the scope of this invention may be made. For example, in place of the Absorber No. 3, which is the pigment iron blue, one-half to 5% of a suitable soluble dye such as naphthol green may be used. Naphthol green may be used in combination with Absorbers No. 1 and 2 to give the optical characteristics shown in FIGURES 5 and 6.

In certain compositions the resin contained may be substituted up to approximately 90% by silicic acid. For example, a mixture of 25% SiO_2 and 75% polyvinyl butyral, together with the absorbers herein disclosed, may be utilized to provide a solvent coating which, upon evaporation and heating, is strongly adherent to glass surfaces, and to some plastics, and which has a hardness superior to most plastic coatings. The silicic acid promotes adhesion by chemically reacting with surfaces, and hardens by cross linking with the resins and absorbers contained therein.

Having thus fully described the invention, what is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A composition for partially absorbing visible and absorbing ultra violet light comprising a clear transparent plastic film-forming solution and a suspension in said solution of from 0.01% to 2% based on the weight of said solution of light absorbing particles, said solution comprising a solvent portion and a solute portion, said solvent portion being composed of from 5 to 25% by weight of slow evaporation rate solvents and the balance intermediate evaporation rate solvents, said solute portion comprising a transparent film-forming plastic material in amount not exceeding its solubility in said solvent portion, said particles having a maximum diameter no greater than about 50 millicrons and an average diameter no greater than about 10 millicrons, said particles being insoluble in said solution and unreactive therewith, said composition being castable as a transparent film substantially free of light scatter, whereby the composition will flow downwardly for long distances to form upon drying a transparent film.

2. A composition according to claim 1, in which the suspended particles are present in amounts of from 0.01% to .5% and in which the composition further contains a soluble ultra violet absorbent dissolved therein.

3. A composition according to claim 1, wherein said slow evaporation rate solvent is selected from the group consisting of xylene, amyl alcohol, methyl-n-amyl ketone, Cellosolve, methyl Cellosolve acetate, cyclohexanone, ethyl lactate, dichloropentane, Cellosolve acetate, di-isobutyl ketone, and mixtures thereof, and said intermediate evaporation rate solvent is selected from the group consisting of n-propyl alcohol, 1-nitropropane, methyl-n-butyl ketone, isobutyl alcohol, amyl acetate, n-butyl ether, xylene, and mixtures thereof.

4. A composition according to claim 1, wherein said light absorbing particles are carbon particles having a maximum diameter less than 50 millimicrons and an average diameter of the order of 9 millimicrons.

5. A composition according to claim 1, wherein said light absorbing particles comprise crystals of Prussian blue.

6. A composition according to claim 1, wherein said light absorbing particles comprise a mixture of carbon particles in amount from about 0.01 to about 2% and Prussian blue particles in amount from about 4.5 to about 18%, and said ultra violet absorber is present in amount not more than about 8%, based on the weight of said composition.

7. A composition according to claim 1, wherein said carbon particles are present in amount from about 0.2 to about 0.6%, said Prussian blue particles are present in amount from about 0.67 to about 2% and said ultra violet absorber is present in amount from about 2 to about 8%, based on the weight of said composition, said composition being castable to a blue, transparent film.

8. A composition according to claim 1, further comprising an infrared absorbent dye.

9. A composition according to claim 8, wherein said infrared absorbent dye is naphthol green in amount from 1/2% to 5% based on the weight of said composition.

References Cited by the Examiner

UNITED STATES PATENTS

2,432,113	12/1947	Marks et al.	88—65 X
2,487,063	11/1949	Marks	156—99
2,544,363	3/1951	Siemons	106—195 X
2,607,705	8/1952	Kumins	260—40 X
2,613,158	10/1952	Walton et al.	260—16 X
2,858,240	10/1958	Turner et al.	
2,876,210	3/1959	Wynn et al.	106—187 X
2,895,955	7/1959	Heseltine et al.	252—300 X
2,947,646	8/1960	Devaney et al.	
3,069,301	12/1962	Buckley et al.	156—99 X

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