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ULTRAVIOLET LIGHT ABSORBING FILM

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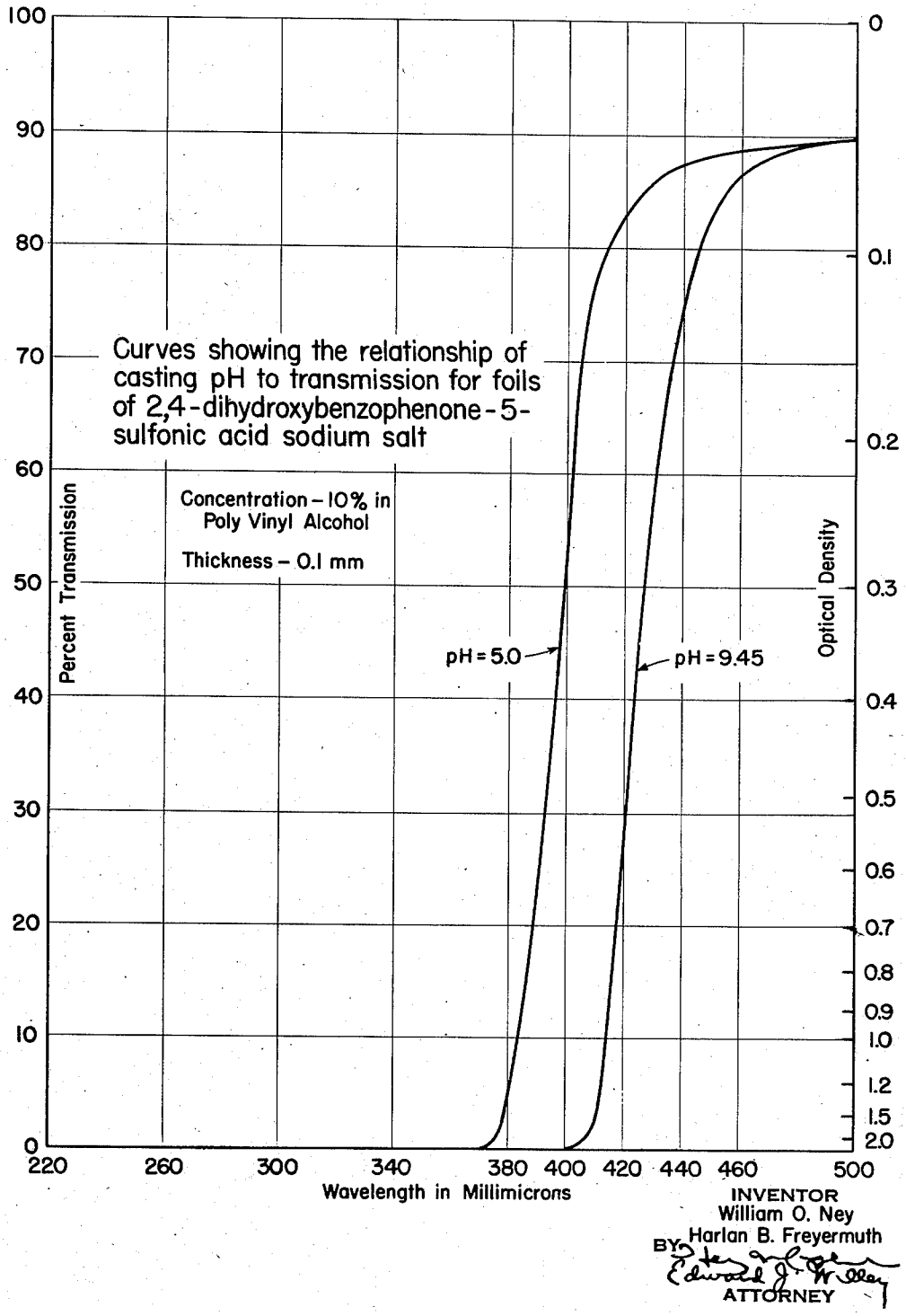

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ULTRAVIOLET LIGHT ABSORBING FILM

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8 Claims. (Cl. 106—125)

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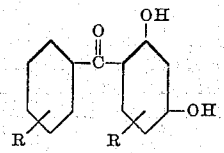
This invention relates to ultraviolet light absorbing films.

It is well known that colored objects such as dyed textiles and the like fade when exposed for prolonged periods to the effect of sunlight. Plastic materials of both the water-soluble and water insoluble type such as gelatin, polyvinyl alcohol, cellulose acetate and the like become colored, usually yellowing, and sometimes brittle and many eventually deteriorate upon exposure to sunlight. The present invention is concerned with ultraviolet light absorbers for the water soluble film forming materials which may be used themselves in packaging, as for example cellophane, or which may be used as a coating upon other materials which fade or deteriorate in sunlight. The absorption of ultraviolet light in materials such as cellophane is particularly important because of the wide spread uses of cellophane as a packaging material, allowing fading or deterioration of the goods which the package contains.

To be most effective, the absorber should be capable of absorbing substantially all of the ultraviolet light within the wave length range 200 to 400 millimicrons and even into the visible range as high as 440 millimicrons.

It is a further object of the present invention to provide a film cast from a water solution of a water soluble film forming plastic containing a water soluble compound particularly adapted to absorbing light having a wave length above about 400 millimicrons.

These and other objects are attained by the present invention wherein a film is cast from a water solution of a water soluble film forming plastic containing a compound having the following general structure:



wherein one R is hydrogen and the other R is an alkaline sulphonate radical.

We have discovered that these compounds when combined with a water soluble plastic in acqueous solution having a pH in the range 5 to 9.5 are unexpectedly compatable and do not crystallize out or make an opaque film as might be expected but rather form a clear film which has the desired light absorption.

The sulphonic acid is neutralized with any of various alkaline material including alkaline earth metals, ammonia, amines such as aliphatic, aromatic, cycloparaffinic and heterocyclic amines,, and preferable alkali metals, alkali hydroxides, or alkaline alkali metal salts (e. g. Na_2CO_3.).

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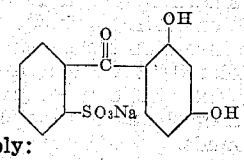
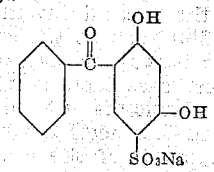
The following compounds are illustrative:



and preferably:



It is an important element of the present invention that the compound have a pH in the range of 5 to 9.5. The above compound, for example, in acid form has a pH of about 1.5 and is unstable and absorbs very little light above 390 millimicrons.

The following examples will serve to illustrate the invention and are preferred embodiments thereof, but are not intended to limit the invention.

Example 1

43 parts of 2,4-dihydroxybenzophenone was added to 200 parts of 20% oleum at a temperature of about 15–20° C. and allowed to stand for about ½ hr. The mixture was added to 1,500 parts of ice whereupon the sulfonated product began to separate out. The mixture was then redissolved by heating to 35° C. and stirred with 5 parts Nuchar and 5 parts filter cell (commercial clarifying agents). After filtering, 1000 parts of a saturated sodium carbonate solution was added. The sodium salt of 2,4-dihydroxybenzophenone - 5 - sulphonic acid precipitated, was filtered, and dried. The pH of aqueous solutions of this salt was about 5.

To 90 parts of a 10% solution of alcohol was added one part of the salt prepared above. The solution, having a pH of 5, was then cast on a glass plate and dried. The clear, colorless film obtained absorbed ultraviolet light in the range of 220 to 400 millimicrons.

Example 2

Ten parts of the sulphonic acid product of Example 1 was dissolved by heating in 100 parts

of water to 80–90° C. To this solution was added an equivalent amount of an aqueous solution of cyclohexyl amine. On cooling, the cyclohexyl amine salt of 2,4-dihydroxybenzophenone precipitated as large, nearly colorless plates (pH of aqueous solution=5).

To 95 parts of the 10% polyvinyl alcohol solution containing sufficient NaOH added to adjust the pH of the solution to 9.45 was added 1 part of cyclohexylamine 2,4-dihydroxybenzophenone-5-sulfonate. The film obtained on casting was clear, pale yellow and had the characteristic of absorbing light in the range 220 to 430 millimicrons.

Example 3

To 90 parts of a 10% aqueous solution of gelatin was added 1.0 part of the sodium salt of 2,4-dihydroxybenzophenone-5-sulfonic acid. A film resembling that the Example 1 was obtained.

Example 4

To 90 parts of a 10% solution of gelatin was added 1.0 part of cyclohexyl amine salt of 2,4-dihydroxybenzophenone-5-sulfonic acid. A film resembling that of Example 2 was obtained.

The graph shown in the drawing is self-explanatory. It demonstrates that the compounds of the present invention absorb substantially all of the ultraviolet light without extending substantially into the visible range and shows the effect of the pH on the absorption characteristics of these compounds.

The film of the present invention may be a self-supported film such as the cellophane used in packaging or it may be used as a protective coating on other bases such as water soluble or water insoluble plastic materials as, for example, photographic cellulose acetate film, glass or the like. The compounds of the present invention are colorless and as such absorb very little visible light and subsequently do not distort the color balance of articles which they may protect. They are useful in photographic filters, sun tan lotions, and cellophane potato chip packages, among other uses.

The compound of Example 1 contains the sulfonic acid group in the substituted (resorcinol) ring because on oxidation, benzoic acid is isolated from the reaction products, which demonstrates that sulfonation does not take place in the other ring.

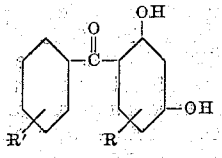
Examples of film forming organic plastic materials which are soluble in the aqueous mediums herein employed, that is aqueous mediums having a pH in the range of 5 to 9.5 include regenerated cellulose, partially hydrolyzed polyvinyl acetate, polyvinyl alcohol, gelatin, carboxymethyl cellulose, hydroxymethyl cellulose, urea-formaldehyde resins, melamine-formaldehyde resins, polyacrylamides, poly (N - hydroxyalkylacrylamide), poly(ethylene glycol monoacrylate), polyvinylmethyl ether, etc.

Control of the pH of the compound of the present invention to keep it in the range pH 5 to 9.5 is important for substantial absorption to 400 to 440 millimicrons and the pH within those limits is substantially proportional to the wave length of light absorbed within the range indicated. Thus the material absorbs substantially all of the light below the visual range while itself being colorless or very pale yellow.

It will be understood that the amount of these compounds used will depend upon the thickness of the supporting film and the pH. In general the higher the pH and the larger the amount of compound the more the curves will extend toward the visible range. At a pH of 5.0 for example, from about 0.0005 to about 0.01 gram of the compound per $cm.^2$ gives satisfactory absorption.

We claim:

1. An improved ultraviolet light absorbing film comprising a film-forming plastic soluble in an aqueous medium having a pH of 5 to 9.5 and a salt of a sulfonic acid, which sulfonic acid has the formula:



wherein one of the radicals R and R' is hydrogen and the other is SO_3H, said salt having a pH in aqueous solution in the range 5 to 9.5.

2. The film of claim 1 wherein R is hydrogen, R' is an ortho-SO_3H radical in the recited structural formula, and the salt is a sodium salt.

3. The film of claim 1 wherein R' is hydrogen, R is an —SO_3H radical in the 5 position in the recited structural formula, and the salt is a sodium salt.

4. The film of claim 1 wherein the said film-forming plastic is regenerated cellulose.

5. The film of claim 1 wherein the said film-forming plastic is polyvinyl alcohol.

6. The film of claim 1 wherein the said film-forming plastic is gelatine.

7. The film of claim 1 wherein the said film-forming plastic is a partially hydrolyzed polyvinyl acetate.

8. The film of claim 1 wherein the said film-forming plastic is hydroxymethyl cellulose.

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