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HAIR SPRAY COMPOSITIONS CONTAINING AN ULTRAVIOLET ABSORBING FILM FORMING COPOLYMER

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ABSTRACT OF THE DISCLOSURE

Aerosol formulations suitable for use as hair spray lacquers comprising an organic solvent solution of an ultraviolet absorbing, film forming copolymer in admixture with a propellant therefor.

This invention relates to the preparation of hair fixing compositions especially suitable for use in aerosol formulations and, more particularly, to the novel film forming polymeric binders contained therein.

In order to be highly effective in aerosol hair spray formulations, the film forming, polymeric binders utilized therein as well as the films derived therefrom must meet a rigid set of requirements. Thus, the binders used in such formulations should be soluble in anhydrous organic solvents; yet the films cast from such hair spray formulations should, ordinarily, either be water soluble or water dispersible in order to facilitate their easy removal from the user's hair. As is readily visualized, this is an unusual combination of properties which is further complicated by the requirement that the binder used in such formulations be completely compatible with the propellants and solvents ordinarily employed therein. Furthermore, the binders used should show little or no tendency to interact with the perfumes or other optional ingredients utilized in hair spray formulations.

In addition, the films cast from either aqueous or organic solvent solutions of these binders should be flexible and yet they should have sufficient strength and elasticity; they should adhere well to hair so as to avoid dusting or flaking off when the hair is subjected to varying stresses; they should readily allow the hair to be recombed; they should maintain a nontacky state despite humid conditions; they should be clear, transparent and glossy and should maintain this clarity on aging; they should possess good anti-static properties; and, they should be easily removable by the use of water and/or soap or shampoo.

An additional property, which assumes greater significance as a result of the ever increasing utilization of hair colorants, is the protection of the hair from the harmful effects of ultraviolet radiation. Thus, for the users of such hair colorants, it would be most desirable that the hair spray formulation be in some way modified to protect the resulting hair spray films and/or the colorants or dyes utilized in the hair coloring process from the undesirable discoloration produced by exposure to sunlight. Such protection can, in fact, be obtained by the use of a so called ultraviolet absorbing compound which serves to absorb those wavelengths of ultra-violet radiation which cause the discoloration effect. However, upon being incorporated into a hair spray formulation, such ultraviolet absorbers must also possess the properties of being non-volatile, non-extractable, and fully compatible with the other components of the system. Furthermore, they must not render the resulting hair spray formulation toxic or in any way harmful to the user.

It is the prime object of this invention to provide a

novel class of film forming copolymers for use, as binders, in hair spray formulations, said copolymers being characterized by their solubility in organic solvents, their compatibility with the halogenated hydrocarbons ordinarily used as aerosol propellants and, in particular, by their ability to protect against ultraviolet radiation. It is a further object to produce hair spray formulations containing novel ultraviolet absorbing, film forming copolymers which exhibit all of the properties noted hereinabove.

Various other objects and advantages of this invention will be apparent upon a reading of the disclosure which follows hereinafter.

We have discovered that by utilizing the novel class of copolymers hereinafter described as the film forming binder component of the hair spray formulations of this invention, all of the previously described requirements for an effective hair spray formulation are met. Particularly significant is the novel protection afforded by these formulations against any discoloration of their own films and/or of any hair colorant present on the user's hair, which results from their exposure to ultraviolet radiation. Of particular significance is the fact that, as will be seen, the protection against the effects of exposure to ultraviolet radiation is provided to our hair spray formulations as a result of the "built-in" presence in their polymeric binders of moieties derived from ultraviolet absorbing compounds. In other words, this protection is not derived from the presence of extraneous additives which may be readily lost from the films derived from these formulations as a result of any surface migration or solvent leaching effects. Furthermore, the fact that no extraneous additive is required will also eliminate any compatibility problems between such additives and the various other components of the hair spray formulation. In addition, these unique ultraviolet absorbing, film forming copolymers are soluble in organic solvents, are completely compatible with aerosol propellants and show little or no tendency to interact with perfumes or other optional ingredients of hair spray lacquer formulations.

The films cast from aqueous or organic solvent solutions of these copolymers are clear and glossy, do not yellow on aging and possess the highly desirable properties of softness and flexibility. In addition, these films are readily water dispersible, thus enabling their quick removal from the hair.

The ultraviolet absorbing, film forming copolymers utilizable as binders in the hair spray formulations of this invention comprise copolymers containing moieties derived from:

(1) At least one comonomer which is an ethylenically unsaturated derivative of a compound capable of absorbing ultraviolet radiation; and,

(2) At least one conventional ethylenically unsaturated comonomer whose presence in the resulting copolymer will permit films to be derived therefrom which are either water soluble or can be readily rendered water soluble by either partial or complete neutralization.

Thus, the above described copolymers may be briefly described as copolymers resulting from the polymerization of at least one ultraviolet absorbing comonomer together with at least one ethylenically unsaturated comonomer which will impart the desired solubility characteristics to the films derived from the resulting copolymer. The latter group of comonomers may thus comprise either comonomers which directly render the copolymer water soluble or acidic comonomers containing one or more available carboxyl groups which make it possible for the resulting copolymer to be neutralized by reaction with an appropriate base in order that it may ultimately exhibit this requisite water solubility. It should be noted that the latter copolymers, i.e. those resulting

from the use of acidic comonomers, may be neutralized prior to their being incorporated into the ultimate hair spray formulation thus permitting them to be removed from the hair merely by rinsing with water. However, if such copolymers are not pre-neutralized, in this manner, their eventual removal may still be readily effected by the application of an alkaline aqueous solution, e.g. soap and water. Furthermore, it should be noted that for purposes of this invention, the term "water solubility" is meant to include both water solubility in its usual meaning as well as water dispersibility wherein the resulting films are sufficiently hydrated and softened by contact with water so as to be easily removed from the hair by the application of water and either soap or a shampoo.

With respect to the ethylenically unsaturated derivatives of compounds capable of absorbing ultraviolet radiation and which are, therefore, capable of being utilized as the ultraviolet absorbing comonomers in the preparation of the copolymers which comprise the novel ultraviolet absorbing, film forming, hair spray binders of this invention, the following groups of monomeric materials may be listed:

(A) The ethylenically unsaturated derivatives of phenyl salicylate, described in U.S. Patent 3,141,903 which are prepared by means of the reaction between an acrylyl or methacrylyl halide with phenyl 2,5-dihydroxy benzoate;

(B) The ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone, described in U.S. Patent 3,162,676 which are prepared by means of the reaction between glycidyl acrylate or methacrylate with either 2,4-dihydroxybenzophenone; 2,2',4-trihydroxybenzophenone; or, 2,2',4,4'-tetrahydroxybenzophenone;

(C) The ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone, described in U.S. Patent 3,202,716 which are prepared by means of the reaction between allyl glycidyl ether or butadiene monoxide with either 2,4-dihydroxybenzophenone; 2,2',4-trihydroxybenzophenone; or 2,2',4,4'-tetrahydroxybenzophenone;

(D) The ethylenically unsaturated derivatives of orthodihydric phenols, described in U.S. Patent 3,156,720 which are prepared by means of the reaction between an ortho-dihydric phenol and either glycidyl acrylate or methacrylate;

(E) The ethylenically unsaturated derivatives of ortho-hydroxy aromatic acids, described in U.S. Patent 3,167,583 which are prepared by means of the reaction between an ortho-hydroxy aromatic acid and either glycidyl acrylate or methacrylate;

(F) The ethylenically unsaturated benzophenone derivatives, described in British Patent 885,986 which are prepared by means of the reaction between acrylyl or methacrylyl chloride and 2,4-dihydroxybenzophenone;

(G) The ethylenically unsaturated amino substituted benzophenone derivatives, described in U.S. Patent 3,120,564 which are prepared by means of the reaction between an amino and further substituted 2-hydroxybenzophenone with an alkenoyl halide;

(H) The ethylenically unsaturated benzotriazole derivatives, described in U.S. Patent 3,072,585 which are prepared by means of the reaction between hydroxy substituted 2-hydroxyphenylbenzotriazoles with chloromethylstyrenes;

(I) The ortho substituted ethylenically unsaturated phenol derivatives, described in British Patent 894,702 which are prepared by means of the reaction between an alpha, beta-unsaturated acid chloride and p-tertiarybutylphenol;

(J) The ethylenically unsaturated benzophenone derivatives, described in U.S. Patent 2,962,533 which are prepared by means of the selective alkenylation of either 2,4-dihydroxybenzophenone; 2,2',4-trihydroxybenzophenone; or 2,2',4,4'-tetrahydroxybenzophenone to replace the hydrogens on the para hydroxyls, but to leave the ortho hydroxyls untouched;

(K) The ethylenically unsaturated benzotriazole derivatives, described in copending application Ser. No. 535,325 filed Mar. 18, 1966, and assigned to the assignee of the subject application which are prepared by means of the reaction between glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether or butadiene monoxide with 2-(2,4-dihydroxyphenyl) benzotriazole; which application is fully incorporated herein.

(L) The ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone described in copending application Ser. No. 224,247, filed Sept. 17, 1962 and assigned to the assignee of the subject application which are prepared by means of the reaction between 2,4-dihydroxybenzophenone and a glycidyl ester of an ethylenically unsaturated carboxylic acid containing at least 4 carbon atoms.

(M) The ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone described in copending application Ser. No. 226,464, filed Sept. 26, 1962 and assigned to the assignee of the subject application which are prepared by means of the reaction between 2-hydroxy-4-methoxy-5-chloromethylbenzophenone with an alkali metal salt of acrylic or methacrylic acid;

(N) The ethylenically unsaturated derivatives of phenyl salicylate, described in copending application Ser. No. 328,485, filed Dec. 6, 1963 and assigned to the assignee of the subject application which are prepared by means of the reaction of an allyl halide with phenyl salicylate; and,

(O) The ortho substituted ethylenically unsaturated phenol derivatives, described in copending application Ser. No. 282,593, filed May 23, 1963 and assigned to the assignee of the subject application which are prepared by the reaction of an ortho-substituted halomethyl salicylic acid with an alkali metal salt of acrylic or methacrylic acid.

The patents and applications listed are to be considered fully incorporated herein.

It is to be noted that all of the above groups of ethylenically unsaturated ultraviolet absorbing compounds fall into one of the following broad categories:

(1) Ethylenically unsaturated derivatives of phenyl salicylate;

(2) Ethylenically unsaturated derivatives of benzophenone;

(3) Ethylenically unsaturated derivatives of phenols wherein the ethylenic unsaturation is substituted ortho to the phenolic hydroxyl group; and

(4) Ethylenically unsaturated derivatives of benzotriazole.

In addition to the information which is presented in the experimental examples, further details relating to detailed preparation of the specific compounds encompassed by the above listed groups may be obtained by reference to the various cited patents. Needless to say, these groups of compounds are to be considered as being merely illustrative inasmuch as any other ethylenically unsaturated derivatives of compounds capable of absorbing ultraviolet radiation are similarly applicable for use as comonomers in preparing our novel polymeric hair spray binders.

As for the conventional ethylenically unsaturated comonomers which are required in the preparation of the ultraviolet absorbing, film forming hair spray binders of this invention, the following list of monomers may be taken as representative thereof:

Vinyl pyrrolidone; vinyl esters such as vinyl acetate; the C_1–C_2 betahydroxyalkyl esters of acrylic and methacrylic acids; the acrylic and methacrylic acid esters of aliphatic alcohols such as methyl, ethyl, propyl, butyl, isobutyl, amyl, hexyl, 2-ethylhexyl, octyl, lauryl and stearyl alcohols.

The following list of monomers are representative of the applicable acidic comonomers which contain at least one available carboxyl group and whose presence in the

resulting copolymer serves to render it alkali soluble or dispersible:

Acrylic acid; methacrylic acid; itaconic acid; crotonic acid; and, the C_1–C_4 alkyl half esters of maleic and fumaric acids such, for example, as methyl hydrogen maleate and butyl hydrogen fumarate; as well as any other acidic monomers which will be uniformly copolymerized with the particular ultraviolet absorbing comonomer whose use is desired by the practitioner.

Also applicable are copolymers of an ultraviolet absorbing comonomer with a vinyl ester; said copolymer thereupon being partially hydrolyzed as, for example, the partially hydrolyzed copolymer of vinyl acetate with any of the above described ultraviolet absorbing comonomers.

In order to provide binders which will function efficiently as ultraviolet absorbers in the novel hair spray formulations of this invention, it is necessary that the copolymer contain from about 0.1 to 15%, by weight, of moieties derived from at least one of the above described ethylenically unsaturated ultraviolet absorbing compounds.

As for the actual prepartion of these polymeric, film forming binders, there may be employed any of the usual vinyl polymerization methods which are well known to those skilled in the art and which are particularly suited for the copolymer whose preparation is desired. Thus, they may be prepared by means of free radical initiated processes utilizing bulk, suspension, solution, or emulsion polymerization techniques.

In any event, the novel polymer film forming binders of this invention, whether prepared by means of bulk, suspension, solution, or emulsion polymerization techniques, or by any other means, are all characterized by their ability to absorb ultraviolet radiation, thus preventing film and/or colorant discoloration, as well as by their solubility in organic solvents and their compatibility with aerosol propellants.

If the polymeric binder is a copolymer containing moieties derived from one or more acidic comonomers, it may, as noted earlier, be desired to partially neutralize the copolymer prior to its incorporation into the hair spray formulation. This may be accomplished by reacting the copolymer with a concentration of an alkaline material which is equivalent on a molar basis to no more than about 175% of the available carboxyl groups on the copolymer. Applicable alkaline materials which may be utilized in this manner include: sodium and potassium hydroxide; ammonia, primary, secondary and tertiary amines; alkanolamines; and, hydroxyamines such as 2-amino-2-methyl-1,3-propanediol.

As previously mentioned, the other essential ingredients of the hair spray formulations of this invention are the solvent and the propellant, in some instances the propellant serving both functions. The preferred solvents are alcohols such as ethanol and isopropanol. In addition to their solubility properties, the prime advantages of these solvents are their ability to dry quickly and their minimal effect on the metal containers ordinarily utilized for these pressurized aerosol formulations. Other solvents which may be used include methylene chloride and 1,1,1-trichloroethane, etc.

Various types of aerosol propellants are well known to those skilled in the art. Thus, the commonly used propellants include trichlorofluoromethane, dichlorodifluoromethane, isobutane and propane, etc., as well as mixtures of the latter propellants. These propellants are readily compatible with the binder-solvent solutions utilized in this invention.

In general, the method for preparing the hair spray formulations of this invention merely involves admixing the ultraviolet absorbing, film forming copolymers with the selected solvent, adding any modifying agents whose presence may be desired, and thereupon combining the resulting solution with the selected aerosol propellant.

Thus, it may be noted that the novel hair spray formulations of this invention will in all cases contain at least these three essential components. The first of the latter components will be what may be termed as the active ingredient comprising one or more of our novel ultraviolet absorbing, film forming copolymers which serves as the binder for the formulation. Secondly, there will be one or more solvents which serve as vehicles for the binder. And, finally, there is the propellant which serves to effect the discharge of the aforedescribed binder and vehicle from the container wherein the formulation is packaged.

With regard to proportions, the final hair spray formulations typically contain the ultraviolet absorbing, film forming polymeric binder in a concentration ranging from about 0.1 to 7%, by weight; the solvent in a concentration ranging from about 8 to 90%, by weight; and, the propellant in a concentration ranging from about 10 to 85%, by weight. The latter proportions should, however, be considered as being merely illustrative inasmuch as it may well be possible to prepare operable formulations having concentrations of components which fall outside the above suggested ranges.

Optional additives may be incorporated into the hair spray formulations of this invention in order to modify certain properties thereof. Among these additives may be included:

Plasticizers such as glycols, phthalate esters, and glycerine; silicones; emollients, lubricants, and penetrants such as lanolin compounds, protein hydrolyzates and other protein derivatives, ethylene oxide adducts, and polyoxyethylene cholesterol; dyes and other colorants; and, perfumes. As previously noted. the polymeric binders of this invention show little or no tendency to interact with such additives.

The resulting hair spray formulations exhibit all of the characteristics required of such a product. Their films are transparent, glossy, flexible, and strong. They possess good anti-static properties, adhere well to hair, are easily removed by soapy water or shampoos, allow the hair to be readily recombed, do not yellow on aging, and do not become tacky when exposed to high humidities. Of primary importance is the fact that the novel air spray formulations of this invention serve to protect both the films derived therefrom and the colorant on the user's hair from the degradative effects and discoloration resulting from their exposure to ultraviolet radiation.

In addition, it should be noted that the unique ultraviolet absorbing, film forming copolymers of this invention are equally as effective when utilized in aqueous or alcoholic hair setting lotions. Such lotions may be directly applied to the hair or they may be sprayed thereon utilizing conventional spray nozzles. The application, in these instances, may take place prior to, during, or after the desired air style has been achieved.

In the following examples, which further illustrate the embodiment of this invention, all parts given are by weight unless otherwise indicated.

Example I

This example illustrates the preparation of a typical hair spray formulation of this invention containing one of our novel ultraviolet absorbing, film forming copolymers as the binder therein.

The particular binder utilized in this formulation was a 5:20:30:20:25 4-methacryloxy-beta-hydroxypropyl ether of 2,4-dihydroxybenzophenone:acrylic acid:methyl acrylate:methyl methacrylate:hydroxypropyl acrylate copolymer which was insoluble in water and completely soluble in soap solution and which was prepared in the form of an ethanol lacquer, containing about 41%, by weight, of resin solids, by means of the solution polymerization procedure described in Example III of U.S. Patent 3,173,893. The ethylenically unsaturated ultraviolet absorbing compound, i.e. the 4-methacryloxy-beta-

hydroxypropyl ether of 2,4-dihydroxybenzophenone, utilized in the preparation of the latter copolymer may be briefly described as an ethylenically unsaturated ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example II of U.S. Patent 3,162,676 which involved the reaction of glycidyl methacrylate with 2,4-dihydroxybenzophenone.

The preparation of the hair spray formulation based on this particular binder was completed by first diluting 7.3 parts of the copolymer lacquer with 22.7 parts of anhydrous ethanol. Thereafter, the completely clear solution was introduced into an aerosol container which had been charged with 70 parts of a 60:40 propellant mixture of trichlorofluoromethane and dichlorodifluoromethane; the resulting system being completely compatible. The container used, typical for these purposes, was a 6 ounce can, filled to internal pressure of 30 pounds per square inch gauge. Actual conditions for filling spray containers are generally of this order of magnitude. It is desirable that a spray be energetically injected for adherence to the hair without disturbing the coiffure.

When utilized, the resulting hair spray formulation deposited a film which was characterized by its clarity, gloss, softness and flexibility. It served to hold the desired hair style in place while also allowing for its recombing. Of great significance was the fact that it was readily removed from the hair by use of an aqueous soap solution. Furthermore, when subjected to ultraviolet radiation, the films derived from this formulation exhibited outstanding resistance to the degradative effects and discoloration normally resulting therefrom.

Example II

This example further illustrates the preparation of hair spray formulations typical of this invention containing ultraviolet absorbing, film copolymers containing moieties, derived from a wide variety of ethylenically unsaturated derivatives of compounds capable of absorbing ultraviolet radiation.

The particular ultraviolet absorbing, film forming copolymers utilized as binders in the various hair spray formulations described in this example were copolymers which contained an ultraviolet absorber comonomer, vinyl acetate, and crotonic acid in a monomer ratio of 5:85:10 and which were prepared in the form of ethanol lacquers containing about 50%, by weight, of resin solids, by means of the solution polymerization procedure described, respectively, in (a) Example III of U.S. Patent 3,173,893; (b) Example I of U.S. Patent 3,173,893; (c) Example VI of U.S. Patent 3,186,968; (d) Example VI of U.S. Patent 3,186,968; (e) Example I of U.S. Patent 3,173,893; (f) Example III of U.S. Patent 3,173,893; (g) Example I of U.S. Patent 3,173,893; (h) Example I of U.S. Patent 3,173,893; (i) Example II of U.S. Patent 3,180,851; (j) Example VI of copending application, Ser. No. 535,325, filed Mar. 18, 1966 and assigned to the assignee of the subject application; (k) Example II of U.S. Patent 3,180,851; (l) Example VI of copending application, Ser. No. 535,325, filed Mar. 18, 1966 and assigned to the assignee of the subject application; and, (m) Example VI of copending application, Ser. No. 535,325, filed Mar. 18, 1966 and assigned to the assignee of the subject application.

The following ethylenically unsaturated ultraviolet absorbing compounds were used in the preparation of the polymeric binders contained in these formulations:

(A) 4-methacryloxy-bete-hydroxypropyl ether of 2,4-dihydroxybenzophenone, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example II of U.S. Patent 3,162,676, which involved the reaction of glycidyl methacrylate with 2,4-dihydroxybenzophenone.

(B) 4-acryloxy-beta-hydroxypropyl ether of 2,4-dihydroxybenzophenone, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example I of U.S. Patent 3,162,676, which involved the reaction of glycidyl acrylate with 2,4-dihydroxybenzophenone.

(C) Phenyl 2-hydroxy-5-methacrylyloxymethyl benzoate, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing phenyl salicylate derivative. It was synthesized by means of the procedure described in Example VI of U.S. Patent 3,141,903, which involved the reaction of phenyl 2-hydroxy-5-chloromethyl benzoate with sodium methacrylate.

(D) Phenyl 2-hydroxy-5-acrylyloxymethyl benzoate, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing phenyl salicylate derivative. It was synthesized by means of the procedure described in Example V of U.S. Patent 3,141,903, which involved the reaction of phenyl 2-hydroxy-5-chloromethyl benzoate with sodium acrylate.

(E) 4-acryloxy-beta-hydroxypropyl ether of 2,2',4-trihydroxybenzophenone, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example III of U.S. Patent 3,162,676, which involved the reaction of glycidyl acrylate with 2,2',4-trihydroxybenzophenone.

(F) 4-methacryloxy-beta-hydroxypropyl ether of 2,2',4-trihydroxybenzophenone, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example III of U.S. Patent 3,162,676, which involved the reaction of glycidyl methacrylate with 2,2',4-trihydroxybenzophenone.

(G) 4-(3-allyloxy-2-hydroxy)propyl ether of 2,4-dihydroxybenzophenone, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example II of U.S. Patent 3,202,716, which involved the reaction of allyl glycidyl ether with 2,4-dihydroxybenzophenone.

(H) 4-(3-hydroxy)butenyl-1 ether of 2,4-dihydroxybenzophenone, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzophenone derivative. It was synthesized by means of the procedure described in Example I of U.S. Patent 3,202,716, which involved the reaction of butadiene monoxide with 2,4-dihydroxybenzophenone.

(I) 2-hydroxy-3-(2-hydroxybenzoyloxy)propyl methacrylate, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing ortho substituted phenol derivative. It was synthesized by means of the procedure described in Example III of U.S. Patent 3,167,583, which involved the reaction of glycidyl methacrylate with salicylic acid.

(J) 4-(3-methacryloxy-2-hydroxypropyl) ether of 2-(2,4-dihydroxyphenyl) benzotriazole, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzotriazole derivative. It was synthesized by means of the procedure described in Example I of copending application, Ser. No. 535,325, filed Mar. 18, 1966 and assigned to the assignee of the subject application, which involved the reaction of glycidyl methacrylate with 2-(2,4-dihydroxyphenyl)benzotriazole.

(K) 2-hydroxy-3-(2-hydroxyphenoxy)propyl acrylate, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing ortho substituted phenol derivative. It was synthesized by means of the procedure described in Example I of U.S. Patent 3,156,720, which involved the reaction of glycidyl acrylate with o-dihydroxybenzene.

(L) 4-(3-acryloxy-2-hydroxypropyl ether of 2-(2,4-dihydroxyphenyl) benzotriazole, which may be briefly described as an ethylenically unsaturated, ultraviolet absorb-

ing benzotriazole derivative. It was synthesized by means of the procedure described in Example I of copending application, Ser. No. 535,325, filed Mar. 18, 1966 and assigned to the assignee of the subject application, which involved the reaction of glycidyl acrylate with 2-(2,4-dihydroxyphenyl) benzotriazole.

(M) 3-(3-methacryloxy-2-hydroxypropyl) ether of 2-(2,3-dihydroxyphenyl) benzotriazole, which may be briefly described as an ethylenically unsaturated, ultraviolet absorbing benzotriazole derivative. It was synthesized by means of the procedure described in Example I of copending application, Ser. No. 535,325, filed Mar. 18, 1966 and assigned to the assignee of the subject application, which involved the reaction of glycidyl methacrylate with 2-(2,3-dihydroxyphenyl) benzotriazole.

The following table describes the composition of the hair spray formulations, wherein copolymers containing each of the above described ethylenically unsaturated, ultra-violet absorbing compounds were present. These formulations were all prepared utilizing the procedure set forth in Example I, hereinabove. The various modifying agents were added to the resin-alcohol solutions prior to the addition of the propellant thereto.

Note that the particular letter, i.e. A, B, C, etc. assigned to each formulation also indicates the specific copolymer component utilized therein. Thus, for example, the copolymer utilized in Formulation A is the copolymer described hereinabove wherein the ultraviolet absorbing comonomer (A), i.e. 4-methacryloxy-beta-hydroxypropyl ether of 2,4-dihydroxybenzophenone, is present.

Formulation	A	B	C	D	E	F	G	H	I	J	K	L	M
Ingredients (parts):													
Solid polymeric binder	3.60	2.40	1.80	2.40	1.80	3.60	2.40	1.80	2.40	1.80	1.80	2.40	1.80
2-amino-2-methyl-1,3-propanediol	0.36	0.20	0.10	0.30	0.18	0.24	0.24	0.18	0.28	0.18	0.18	0.24	0.09
Isopropyl myristate	0.10								0.10				
Polymethyl polysiloxane	0.10	0.10	0.10	0.10	0.10		0.10			0.10	0.10		0.09
Butyl benzyl phthalate			0.18			0.10							
Acetylated lanolin	0.20						0.15	0.10		0.10		0.20	0.09
Oleyl alcohol		0.10		0.20		0.10					0.15		
Perfume	0.20	0.15	0.10	0.15	0.10	0.20	0.15	0.10	0.50	0.10	0.10	0.15	0.09
Anhydrous ethanol	15.44	37.05	27.72	26.85	27.82	35.76	16.96	27.82	16.72	27.72	27.67	17.01	27.84
Trichlorofluoromethane (propellant mix) with Dichlorodifluoromethane	40.00	36.00	42.00	35.00	42.00	36.00	48.00	42.00	48.00	35.00	42.00	48.00	42.00
	40.00	24.00	28.00	35.00	28.00	24.00	32.00	28.00	32.00	35.00	28.00	32.00	28.00

All of these formulations provided transparent, glossy, flexible films which firmly adhered to hair but which were, nonetheless, readily removed by washing with soap solutions. In addition, these films retained their original nontacky state, were resistant to the build-up of electrostatic charges, and maintained their effective holding power despite frequent combing. Furthermore, they exhibited outstanding resistance to the degradative effects and discoloration of ultraviolet radiation.

Example III

This example illustrates the unique resistance to ultraviolet radiation exhibited by the novel hair spray binder resins of this invention. It further illustrates the advantages of having the ultraviolet absorber present as an integral component of the film forming polymeric binder.

In this example, resistance to ultraviolet radiation was determined by the utilization of the following test procedure:

A total of 20 parts of a commercially available hair dye was dissolved in an acetone lacquer containing 40%, by weight, of polymethyl methacrylate. Films having a 1½ mil wet thickness were then cast from this tinted lacquer; these films serving as the control for the determinations.

A sample of a 0.6 mil thick film derived from a number of the novel binders used in the hair spray formulations of this invention were then cast, respectively, over samples of the blue tinted control films. An unprotected control as well as the various film laminates comprising a control coated with the binder copolymer were then exposed to the equivalent of 63 hours of direct sunlight by being placed, at a distance of two feet, from a mercury vapor photochemical lamp which was enclosed, together with the films, in a ventilated light proof cabinet for a period of 4½ hours.

The effect of this light source upon the various protected and unprotected control films was determined, with respect to any color change which had occurred, by measuring their reflectance both before and after exposure with the use of a Photovolt Reflectometer, Model No. 610; the latter being a device which records proportionately higher readings with the increasing yellowing, or other discoloration, of the particular samples being evaluated.

The total color change after exposure is expressed in MacAdam units (ΔA), with the protection coefficient (PC) of each film being determined by the equation

$$PC=1-\frac{\Delta A_1}{\Delta A_o}$$

wherein A_o is the color change recorded for the unprotected control and A_1 is the color change recorded for the protected control, i.e. a laminate. Superior protection is indicated by high PC values and low ΔA values.

The results of the various determinations are presented in the following table:

Test specimen	ΔA	PC
(1) Control (i.e. unprotected, unlaminated, blue tinted film of polymethylmethacrylate)	19.5	------
(2) Laminate comprising a base coat of the control with a top coat of a 90:10 vinyl acetate:crotonic acid copolymer	15.0	0.23
(3) Laminate comprising a base coat of the control with a top coat of a 90:10 vinyl acetate:crotonic acid copolymer to which has been added, prior to casting, 5%, by weight, of 2,2',4,4'-tetrahydroxybenzophenone	16.5	0.15
(4) Laminate comprising a base coat of the control with a top coat of polymeric binder IIB (binder described in Example ii, hereinabove, comprising a copolymer of 4-acryloxy-beta-hydroxypropyl ether of 2,4-dihydroxybenzophenone, vinyl acetate, and crotonic acid in a monomer ratio of 5:85:10)	5.0	0.75

The above data clearly indicate the excellent protection against ultraviolet radiation afforded by the ultraviolet absorbing, film forming binders utilized in the novel hair spray formulations of this invention. It further indicates the substantial improvement achieved as a result of having the ultraviolet absorber present as an integral part of the polymeric binder molecule as compared to test specimen (3) wherein the ultraviolet absorber was present in the form of an extraneous additive.

Summarizing, it is thus seen that this invention provides for the preparation of novel hair spray formulations which are characterized by their outstanding resistance to ultraviolet radiation, their excellent holding power as well as by the fact that they are readily removable.

What is claimed is:

1. An aerosol formulation suitable for use as hair spray lacquer comprising a solution in an organic solvent selected from the group consisting of ethanol, isopropanol, methylene chloride and 1,1,1-trichloroethane of: (A) 0.1–7% by weight of an ultraviolet absorbing, film forming copolymer which comprises from about 0.1 to 15%, by weight, of moieties derived from: (1) at least one ethylenically unsaturated ultraviolet absorbing compound selected from the group consisting of the ethylenically unsaturated derivatives of phenyl salicylate comprising the reaction product of phenyl salicylate with a reagent selected from the group consisting of the acrylyl, methacrylyl and allyl halides; the ethylenically unsaturated derivatives of benzophenone comprising the reaction products of a benzophenone intermediate selected from the group consisting of 2,4-dihydroxybenzophenone, 2,2',4-trihydroxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone with a reagent selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and butadiene monoxide; the ethylenically unsaturated derivatives of orthodihydric phenols comprising the reaction products of an orthodihydric phenol and a reagent selected from the group consisting of glycidyl acrylate and methacrylate; the ethylenically unsaturated derivatives of ortho-hydroxy aromatic acids comprising the reaction products of an ortho-hydroxy aromatic acid with a reagent selected from the group consisting of glycidyl acrylate and methacrylate; the ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone comprising the reaction products of 2,4-dihydroxybenzophenone with a reagent selected from the group consisting of acrylyl and methacrylyl chloride; the ethylenically unsaturated amino substituted benzophenone derivatives comprising the reaction products of an alkenoyl halide with an amino substituted 2-hydroxybenzophenone; the ethylenically unsaturated benzotriazole derivatives comprising the reaction products of a chloromethylstyrene and a hydroxy substituted 2-hydroxyphenylbenzotriazole; the ethylenically unsaturated phenol derivatives comprising the reaction products of an alpha, beta-ethylenically unsaturated acid chloride and p-tertiary-butylphenol; the ethylenically unsaturated benzophenone derivatives comprising the reaction products resulting from the alkenylation of a benzophenone intermediate selected from the group consisting of 2,4-dihydroxybenzophenone, 2,2',4-trihydroxybenzophenone and 2,2',4,4' - tetrahydroxybenzophenone wherein the resulting reaction products have the hydrogen atoms on their para-hydroxyl groups replaced with alkenyl groups; the ethylenically unsaturated derivatives of benzotriazole comprising the reaction products of 2-(2,4-dihydroxyphenyl) benzotriazole with a reagent selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and butadiene monoxide; the ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone comprising the reaction products of 2,4-dihydroxybenzophenone with a glycidyl ester of an ethylenically unsaturated carboxylic acid containing at least 4 carbon atoms; the ethylenically unsaturated derivatives of benzophenone comprising the reaction products of 2-hydroxy - 4 - methoxy-5-chloromethylbenzophenone and an alkali metal salt of acid selected from the group consisting of acrylic and methacrylic acids; the ortho-substituted ethylenically unsaturated phenol derivatives comprising the reaction products of an ortho-substituted halomethyl salicylic acid with an alkali metal salt of an acid selected from the group consisting of acrylic and methacrylic acids; along with: (2) moieties derived from at least one conventional comonomer selected from the group consisting of vinyl pyrrolidone; vinyl acetate; the C_1–C_2 beta-hydroxyalkyl esters of acrylic and methacrylic acids; the acrylic and methacrylic acid esters of aliphatic alcohols; acrylic acid; methacrylic acid; itaconic acid; crotonic acid; and, the C_1–C_4 alkyl half esters of maleic and fumaric acid; and (B) a propellant which is compatible with said copolymer selected from the group consisting of trichlorofluoromethane, dichlorodifluoromethane, isobutane and propane.

2. A method for the protection of artifically colored hair against discoloration resulting from exposure to ultraviolet radiation, said method comprising applying to the hair an aerosol formulation comprising a solution in an organic solvent selected from the group consisting of ethanol, isopropanol, methylene chloride and 1,1,1-trichloroethane of: (A) 0.1–7% by weight of an ultraviolet absorbing, film forming copolymer which comprises from about 0.1 to 15%, by weight, of moieties derived from: (1) at least one ethylenically unsaturated ultraviolet absorbing compound selected from the group consisting of the ethylenically unsaturated derivatives of phenyl salicylate comprising the reaction products of phenyl salicylate with a reagent selected from the group consisting of the acrylyl, methacrylyl and allyl halides; the ethylenically unsaturated derivatives of benzophenone comprising the reaction products of a benzophenone intermediate selected from the group consisting of 2,4-dihydroxybenzophenone, 2,2',4 - trihydroxybenzophenone and 2,2',4,4' - tetrahydroxybenzophenone with a reagent selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and butadiene monoxide; the ethylenically unsaturated derivatives of ortho-dihydric phenols comprising the reaction products of an ortho-dihydric phenol and a reagent selected from the group consisting of glycidyl acrylate and methacrylate; the ethylenically unsaturated derivatives of ortho-hydroxy aromatic acids comprising the reaction products of an ortho-hydroxy aromatic acid with a reagent selected from the group consisting of glycidyl acrylate and methacrylate; the ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone comprising the reaction products of 2,4-dihydroxybenzophenone with a reagent selected from the group consisting of acrylyl and methacrylyl chloride; the ethylenically unsaturated amino substituted benzophenone derivatives comprising the reaction products of an alkenoyl halide with an amino substituted 2-hydroxybenzophenone; the ethylenically unsaturated benzotriazole derivatives comprising the reaction products of a chloromethylstyrene and a hydroxy substituted 2-hydroxyphenylbenzotriazole; the ethylenically unsaturated phenol derivatives comprising the reaction products of an alpha, beta-ethylenically unsaturated acid chloride and p-tertiary-butylphenol; the ethylenically unsaturated benzophenone derivatives comprising the reaction products resulting from the alkenylation of a benzophenone intermediate selected from the group consisting of 2,4-dihydroxybenzophenone, 2,2',4-trihydroxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone wherein the resulting reaction products have the hydrogen atoms on their para-hydroxyl groups replaced with alkenyl groups; the ethylenically unsaturated derivatives of benzotriazole comprising the reaction products of 2-(2,4-dihydroxyphenyl) benzotriazole with a reagent selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and butadiene monoxide; the ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone comprising the reaction products of 2,4-dihydroxybenzophenone with a glycidyl ester of an ethylenically unsaturated carboxylic acid containing at least 4 carbon atoms; the ethylenically unsaturated derivatives of benzophenone comprising the reaction products of 2-hydroxy-4-methoxy - 5 - chloromethylbenzophenone and an alkali metal salt of an acid selected from the group consisting of acrylic and methacrylic acids; the ortho-substituted ethylenically unsaturated phenol derivatives comprising the reaction products of an ortho-substituted halomethyl salicylic acid with an alkali metal salt

of an acid selected from the group consisting of acrylic and methacrylic acids; along with: (2) moieties derived from at least one conventional comonomer selected from the group consisting of vinyl pyrrolidone; vinyl acetate; the C_1–C_2 beta-hydroxyalkyl esters of acrylic and methacrylic acids; the acrylic and methacrylic acid esters of aliphatic alcohols; acrylic acid; methacrylic acid; itaconic acid; crotonic acid; and the C_1–C_4 alkyl half esters of maleic and fumaric acid; and, (B) a propellant which is compatible with said copolymer selected from the group consisting of trichlorofluoromethane, dichlorodifluoromethane, isobutane and propane; the solid films obtained after evaporation of said organic solvent thereby serving to provide the desired protection.

3. A method for holding the hair in place which comprises spraying onto the hair a solution in an organic solvent selected from the group consisting of ethanol, isopropanol, methylene chloride and 1,1,1-trichloroethane of: (A) 0.1–7% by weight of an ultraviolet absorbing, film forming copolymer which comprises from about 0.1 to 15%, by weight, of moieties derived from: (1) at least one ethylenically unsaturated ultraviolet absorbing compound selected from the group consisting of the ethylenically unsaturated derivatives of phenyl salicylate comprising the reaction products of phenyl salicylate with a reagent selected from the group consisting of the acrylyl, methacrylyl and allyl halides; the ethylenically unsaturated derivatives of benzophenone comprising the reaction products of a benzophenone intermediate selected from the group consisting of 2,4-dihydroxybenzophenone, 2,2',4-trihydroxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone with a reagent selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and butadiene monoxide; the ethylenically unsaturated derivatives of ortho-dihydric phenols comprising the reaction products of an ortho-dihydric phenol and a reagent selected from the group consisting of glycidyl acrylate and methacrylate; the ethylenically unsaturated derivatives of ortho-hydroxy aromatic acids comprising the reaction products of an ortho-hydroxy aromatic acid with a reagent selected from the group consisting of glycidyl acrylate and methacrylate; the ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone comprising the reaction products of 2,4-dihydroxybenzophenone with a reagent selected from the group consisting of acrylyl and methacrylyl chloride; the ethylenically unsaturated amino substituted benzophenone derivatives comprising the reaction products of an alkenoyl halide with an amino substituted 2-hydroxybenzophenone; the ethylenically unsaturated benzotriazole derivatives comprising the reaction products of a chloromethylstyrene and a hydroxy substituted 2-hydroxyphenylbenzotriazole; the ethylenically unsaturated phenol derivatives comprising the reaction products of an alpha, beta-ethylenically unsaturated acid chloride and p-tertiary-butylphenol; the ethylenically unsaturated benzophenone derivatives comprising the reaction products resulting from the alkenylation of a benzophenone intermediate selected from the group consisting of 2,4-dihydroxybenzophenone, 2,2',4-trihydroxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone wherein the resulting reaction products have the hydrogen atoms on their para-hydroxyl groups replaced with alkenyl groups; the ethylenically unsaturated derivatives of benzotriazole comprising the reaction products of 2-(2,4-dihydroxyphenyl) benzotriazole with a reagent selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether and butadiene monoxide; the ethylenically unsaturated derivatives of 2,4-dihydroxybenzophenone comprising the reaction products of 2,4-dihydroxybenzophenone with a glycidyl ester of an ethylenically unsaturated carboxylic acid containing at least 4 carbon atoms; the ethylenically unsaturated derivatives of benzophenone comprising the reaction products of 2-hydroxy-4-methoxy - 5 - chloromethylbenzophenone and an alkali metal salt of acid selected from the group consisting of acrylic and methacrylic acids; the ortho-substituted ethylenically unsaturated phenol derivatives comprising the reaction products of an ortho-substituted halomethyl salicyclic acid with an alkali metal salt of an acid selected from the group consisting of acrylic and methacrylic acids; along with (2) moieties derived from at least one conventional comonomer selected from the group consisting of vinyl pyrrolidone; vinyl acetate; the C_1–C_2 beta-hydroxyalkyl esters of acrylic and methacrylic acids; the acrylic and methacrylic acid esters of aliphatic alcohols; acrylic acid; methacrylic acid; itaconic acid; crotonic acid; and the C_1–C_4 alkyl half esters of maleic and fumaric acid; and (B) a propellant which is compatible with said copolymer selected from the group consisting of trichlorofluoromethane, dichlorodifluoromethane, isobutane and propane; the solid films obtained after evaporation of the organic solvent component serving to hold the hair in the position into which it had previously been arranged.

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