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3,827,959

PROCESS FOR PHOTOPOLYMERIZATION WITH CARBONYLATED PHENYL NUCLEAR SULFONYL CHLORIDE SENSITIZER

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No Drawing. Filed Jan. 12, 1973, Ser. No. 323,032

Int. Cl. C08d 1/00; C08f 1/16

U.S. Cl. 204—159.24

4 Claims

ABSTRACT OF THE DISCLOSURE

U.V. polymerization of a photopolymerizable vehicle is improved by incorporating into the vehicle about 0.5–5% by weight of a carbonylated phenyl nuclear sulfonyl chloride.

CROSS-REFERENCE TO RELATED APPLICATIONS

The present patent application is related to my copending patent application bearing the identical title, and having the identical filing date, i.e., Jan. 12, 1973, and identified with Ser. No. 323,086.

BACKGROUND OF THE INVENTION

This invention relates to an improvement in process for polymerizing (curing) a photopolymerizable vehicle by exposure of same to U.V. radiation. "Curing" herein connotes polymerization and hardening to obtain a product that is practical for ordinary use and normally is tack-free.

The vehicle used herein is the binder for a film in the nature of a paint, varnish, enamel, lacquer, stain, filler or ink. The polymerized product can be a clear one, optionally tinted, or an opaque one, both in a variety of colors for the purpose of protecting, decorating, and/or applying a message on a substrate. For convenience herein the binding vehicle alone for polymerization and such vehicle compounded with other ingredients will be referred to from time to time herein as a "paint." This paint can be a fluent, liquid phase-continuous material or a powdery mixture. It can have, if, desired, opacifying pigment, added colorants and fillers, in conjunction with such binding vehicle. Such paint also can have various other conventional additives such as pesticides, odorants, flow-control agents, bubble breakers, defoamers, plasticizers, intercoat adhesion-promoters, and other ingredients conventional in surface coating films.

Conventional convection ovens and infrared sources have been used to cure (polymerize) binders in surface coating or decorating films and inks, often with the assistance of a catalyst in such deposit. More recently ultraviolet (U.V.) wave energy curing of such binders (vehicles) has been suggested using suitable U.V. sensitizers for initiating photopolymerization at wave lengths in the U.V. spectrum that are transmittable through a quartz or other transparent window, generally such range understood as lying between about 1600 Å. and about 4000 Å.

Typical U.V. emitters for such curing include ones such as the plasma arc torch described in U.S. Pat. 3,364,387, various electric arc lamps, and even lasers having a lasing output in the U.V. spectrum range (as shown in the copending U.S. patent application of deSouza and Buhoveckey, U.S. Ser. No. 189,254). The subject matter of that application and U.S. Pat. 3,364,387 are incorporated herein by reference.

Advantages of the instant invention over prior proposals include especially economical and efficient utilization of U.V. energy, particularly that in wave lengths between about 3200 Å. and 4000 Å. to perform "cold"

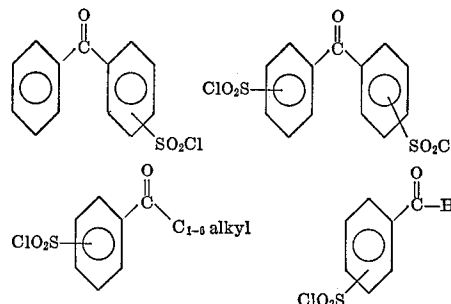
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polymerization (curing) of the vehicle at quite high speed with attendant suppression of losses due to volatilization of components of paint, suppression of discoloration or degradation of the resulting deposit (which can be generally considered a film) and avoidance of shrinkage and distortion (the preservation of dimensional stability) and suppression of degradation of the substrate to which the vehicle deposited is applied, particularly when such substrate is a plastic, or paper, or fabric.

SUMMARY OF THE INVENTION

The instant invention is an improvement in process for polymerizing a U.V. photopolymerizable vehicle by exposure to U.V. radiation. The improvement comprises incorporating into said vehicle about 0.5–5% by weight (and advantageously about 0.5–2% by weight (of the vehicle) of a carbonylated phenyl nuclear sulfonyl chloride or a mixture of same.

This sulfonyl chloride material can be thought of as a U.V. sensitizer or catalyst for assisting said photopolymerization. Such sulfonyl chloride can be incorporated into the vehicle by blending therewith. The sulfonyl chloride can have a structure of the following types (wherein, in addition to single or multiple chlorosulfonation, one or more hydrogen atoms up to 4 on each phenyl nucleus can be replaced with C_{1–6} alkyl or alkoxy groups, or even with halogenated methyl groups, said halogenated methyl groups being CH₂X, CHX₂, and CX₃ with X indicating chlorine, bromine, or iodine):



Monochlorosulfonation of such compounds appears adequate, and thus is preferred for efficiency and economy. There appears to be no particular significance attached to the position of the sulfonyl chloride radical in relation to the carbonyl group. Experiments have shown no critical aspects attributed to any one isomer of sulfonyl chloride. Thus, as photosensitizers, meta-benzophenone monosulfonyl chloride, meta-acetophenone monosulfonyl chloride, and meta-benzaldehyde monosulfonyl chloride work as well as other position isomers. Similarly, the effectiveness of sensitizers containing multiple sulfonyl chlorides is comparable for all isomers.

A convenient way to prepare such sulfonyl chloride materials is to react benzophenone, benzaldehyde, or a lower alkyl phenyl ketone, or their nuclear-substituted derivatives with chlorosulfonic acid in excess of the stoichiometric amount needed for the particular extent of chlorosulfonation desired, heating to about 100° C. for an hour (or even more drastic where plural chlorosulfonation is desired), pouring the reaction product on ice, then separating the organic material from the resulting aqueous layer. Normally solid sulfonyl chloride products are most easily filtered off, and normally liquid ones decanted, but other conventional separation techniques can be used where necessary or desirable.

Frequently the needed proportion of instant sulfonyl chloride sensitizer also can be incorporated directly into the vehicle as a unit of a further polymerizable monomer, oligomer, prepolymer, or polymer vehicle. In such instance, for example, the sulfonyl chloride compound has

a reactable functional group on it such as a carboxyl group or a hydroxyl group. Typically, then, such sulfonyl chloride compound can be made to react with a further polymerizable material, e.g., glycidyl acrylate, either in monomeric form or already part of a preformed prepolymer or oligomer.

Typically the vehicles can constitute the entire deposit or a binder for solids to yield a cured product in the nature of a paint, varnish, enamel, lacquer, stain, or ink. Usually the vehicles are fluid at ordinary operation temperature (between about 30° F. and about 300° F. and advantageously between ordinary room temperature and about 180° F.), and when polymerized by the U.V. radiation, give a tack-free film or deposit that is durable enough for ordinary handling. In the cured state such vehicle is resinous or polymeric in nature, usually cross-linked. Uncured for application to a substrate or uncured on such substrate, such vehicle consists essentially of a monomer or mixture of monomers, or a further polymerizable oligomer, prepolymer, resin, or mixture of same, or a resinous material dispersed or dissolved in a solvent that is copolymerizable therewith. Such solvent ordinarily is monomeric, but can be an oligomer (i.e. up to 4 monomer units connected) or prepolymer (mol weight rarely above about 2000). Oligomers and prepolymers should be understood herein as being polymeric in nature.

In the main such vehicles or binders are those which also are conventionally polymerizable by free radical-induced addition polymerization using peroxy or azo catalysis or a redox system. Alternatively, however, the binders can be a fluent material wherein the ultraviolet wave energy causes photochemical generation of a catalytic material or effects a rearrangement which starts a polymerization that continues until a usually polymerized deposit results. The useful vehicles can be polymeric, monomeric, or a mixture, especially those exhibiting polymerizable vinyl, acrylic, allylic, mercaptan, fumaric, maleic, or like unsaturated functionality. Reactive polymeric types include unsaturated polyesters, acrylics, epoxies, urethanes, and silicones. Representative polymeric vehicles include those derived from the reaction of dibasic acids or their anhydrides with polyols. For example, equimolar amounts of maleic anhydride and phthalic anhydride can be reacted with propylene glycol in slight excess to form an unsaturated polyester which can be extended with styrene to a pre-selected value of non-volatiles (n.v.), generally between 50 and 80% n.v. The polyester resin thus prepared has an acid number of about 60 and less. Of course, fumaric acid can be substituted easily for the maleic anhydride. Similarly, propylene oxide can be substituted for the major portion of propylene glycol. Also instead of styrene other active monomers such as hydroxyethyl-acrylate can be used, usually up to about 50% by weight.

As to acrylic and other polymers, they are trimethylolpropane triacrylate, pentaerythritol triacrylate, ethylene-glycol diacrylate, diacrylic acid adduct of the diglycidyl ether of bisphenol A (DER 332 diacrylate), a di- or triisocyanate reacted with a hydroxy containing acrylate such as hydroxyethyl or hydroxypropyl acrylate.

Reactive monomer types include a variety of acrylates such as hydroxyethyl, cyclohexyl, hydroxypropyl, 2-ethylhexyl, benzyl, phenoxyethoxy, lower alkoxyethoxy, tetrahydrofurfuryl, similar acrylates, and also N-vinyl pyrrolidone, vinyl acetate, vinyl acetate-butyrate, styrene and substituted styrenes.

The instant sulfonyl chloride sensitizers are useful by themselves or in admixture with other sensitizers that are conventional such as benzoin, benzoin ethers, oxime ethers, and phosphines. Additionally, to enhance cure throughout the vehicle when the vehicle temperature is substantially above about 100° F. and such vehicle is particularly susceptible to such catalysis, a minute proportion of a peroxy or like free-radical catalyst can be used.

Not only is the speed of U.V. curing quite good using the present sulfonyl chloride sensitizers, but also the depth of cure is quite practical so that the resultant polymerized deposit resists scratching or disruption when first ostensibly "dry" on the surface. Curing can continue on stored pieces. Typical film thickness for the deposit can be about 0.1 to as high as 10 mils or even substantially higher, e.g., 30-50 mils. Preferred cured deposits are continuous films, but decorative or message-transmitting ones need not be.

Typically the substrate workpieces coated with the uncured deposit or deposits are passed under a U.V. -providing light beam by a conveyor. The substrate being coated can be metal, mineral, glass, wood, paper, plastic, fabric, ceramic, etc.

Many useful pigments can be incorporated, in modest proportions, into the vehicle without much deleterious effects. Thus, opacifying pigments such as zinc oxide can be used quite well. Titania, e.g., anatase and particularly rutile, makes for a much more difficult film to cure by U.V. radiation, but such opacifying pigmentation can be used. Other filler materials and coloring pigments such as basic lead sulfate, magnesium silicate, silica, clays, wollastonite, talcs, mica, chromates, iron pigments, wood flour, microballoons, hard polymer particles, and even reinforcing glass fiber or flake also are suitable in the vehicle to make a paint. Ordinarily it is most desirable to use pigments which do not absorb a great deal of U.V. wavelength in the same region of the U.V. spectrum as is absorbed by the instant sulfonyl chloride sensitizers. However, by use of adjunct energy-transferring, U.V.-sensitizing materials such as Michler's ketone in the sensitizing mixture, sufficient energy transfer often can be obtained to activate the instant sulfonyl chloride and enhance the curing of pigmented systems. The wave length of the U.V. source should not be too similar to or close to the wavelength absorbed by the pigment in the U.V. range for best advantage of the irradiation process. Pigmented or filled films for the process preferably are no more than about a mil thick and generally about 0.1-0.5 mil thick, maximum, for efficiency and economy of curing.

Where it is desirable to induce fusion or flow in a "wet" (uncured) paint deposit such as a powder, followed by a polymerizing cure of the type available by use of the instant improvement, it can be advantageous to first warm the deposit or substrate by a conventional method; e.g., forced or natural convection, electrical induction, or with a source of infrared energy, then follow this with the U.V. radiation for cure.

The following examples show ways in which this invention has been practiced, but should not be construed as limiting it. Unless otherwise specifically stated herein, all parts are parts by weight, all percentages are weight percentages, and all temperatures are in degrees Fahrenheit. Where the binder being cured is of the type normally curable by free-radical polymerization, it is sometimes advantageous for completeness of cure and speed to maintain a substantially inert atmosphere above the irradiated workpiece; e.g., by a purge of nitrogen or other inert gas, but this is not required in all situations.

EXAMPLE 1

A "clear" coating of 1/3 part melamine acrylate, 1/3 part hydroxyethyl acrylate, and 1/3 part of the adduct described below is the vehicle for test curing using a plasma arc radiation unit. The special adduct is the reaction product of one mol of isophorone diisocyanate and 2 mols of hydroxyethyl acrylate.

The curing apparatus is an intense radiation torch (plasma arc) optically directed by a reflector system to irradiate a fresh painted flat aluminum work piece passing below a rectangular irradiating window on an enclosed horizontal conveyor moving at various line speeds (providing about 0.2 second or irradiation at 100 feet a minute and 0.1 second of irradiation at 200 feet a min-

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ute). The atmosphere around the workpiece during its irradiation is kept essentially inert by purging it with nitrogen. Radiation energy supplied by such apparatus at the workpiece surface is about 35 kilowatts per square foot with slightly less than about 6 kilowatts per square foot thereof being in the U.V. spectrum. Such sort of torch is described in U.S. Pat. 3,646,387.

The above "clear" coating is applied to the aluminum workpiece (panel) as a film of about 0.4 mil thickness utilizing a wound wire rod #8. The coated panel is subjected to the radiation emitted by the apparatus described but the film does not cure completely even when exposure at line speed of 100 feet per minute is continued for 150 times (total actual exposure time is 30 seconds). Incomplete cure of the film is recognized by being tacky to the touch.

The vehicle is dosed with 2% by weight of meta-benzophenone mono-sulfonyl chloride well mixed in. The sensitized coating is spread at about 0.4 mil thick on the aluminum test panel and is cured at room temperature by subjecting it to the apparatus as above described. At 100-200 feet per minute line speed the vehicle cures tack-free and has a good scratch resistance to the fingernail, indicating good cure throughout the film depth.

EXAMPLE 2

In this operation the same apparatus, operation, and vehicle of Example 1 are used, except that 2% meta-acetophenone sulfonyl chloride is used. The results are substantially the same.

EXAMPLE 3

In this operation the same apparatus, operation, and vehicle of Example 1 are used, except that 2% meta-benzaldehyde sulfonyl chloride is used. The results are approximately the same as Example 1.

EXAMPLE 4

In this example, the same apparatus, operation, and vehicle of Example 1 are used except for the sensitizer. Rather than the meta-substituted benzophenone a 2% isomeric mixture comprising ortho-, meta- and para-benzophenone sulfonyl chlorides is incorporated into the vehicle with the results being substantially the same as in the preceding examples.

EXAMPLE 5

Similar to Example 4 a 2% mixture comprising ortho-, meta- and para-substituted benzaldehyde sulfonyl chlorides is used instead of the meta-substituted compound with substantially the same results.

EXAMPLE 6

Similar to Example 4 a 2% mixture comprising ortho-, meta- and para-substituted acetophenone sulfonyl chlorides is used in place of the meta-substituted compound without any noticeable change in the results.

EXAMPLE 7

A "clear" vehicle is prepared from $\frac{1}{3}$ part pentaerythritol triacrylate, $\frac{1}{3}$ part hydroxyethyl acrylate, and $\frac{1}{3}$ the adduct formed by reacting one mol of toluenediisocyanate with 2 mols of hydroxyethyl acrylate.

The curing procedure is carried out in the same manner described in Example 1. Without the incorporation of any sensitizers no curing (hardening) of the coated film (0.5 mil) is observed even with repeated exposures to the U.V. source. (Panels coated with the "clear" vehicle to about 0.5 mil thickness are passed under the U.V. radiation source at line speeds of 100 feet per minute for 100 consecutive times without any observable curing.)

Monosubstituted sulfonyl chlorides of benzophenone, acetophenone, and benzaldehyde are each incorporated into the clear vehicle to the extent of 2% by weight. The dosed vehicles are each applied to aluminum panels in films of about 0.5 mil thick. The coated panels are then

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passed under the U.V. radiation source at a line speed of 100 feet per minute (exposure time is 0.2 sec.). Films are cured completely and throughout.

The above-described monosubstituted sulfonyl chlorides refer to the isomeric mixture of each sensitizer.

EXAMPLE 8

A "clear" vehicle is prepared from $\frac{1}{2}$ tri-methylolpropane and $\frac{1}{2}$ 2-ethylhexyacrylate. Into said vehicle is incorporated 2% bromomethylbenzophenone a well-known sensitizer. The vehicle without any sensitizer and the sensitized vehicle are applied to panels and irradiated in the same manner described in Example 1. The vehicle by itself does not appear to cure with repeated exposures at line speed of 100 feet per minute. The dosed vehicle, however, does show some limited curing after one exposure but is still greasy in appearance and tacky to the touch. Only after several consecutive exposures at the same line speed does curing improve. The conclusion is that bromomethyl benzophenone would not be adequate.

EXAMPLE 9

To the same vehicle of Example 8 there is added 2% meta-benzophenone mono-sulfonyl chloride. Treated in the manner described in Example 1, the film shows complete and hard cure in one exposure at line speed of 200 feet per minute.

EXAMPLE 10

Instead of the 2% meta-benzophenone a mono-sulfonyl chloride of Example 9, 2% meta-acetophenone monosulfonyl chloride is used with substantially the same results.

EXAMPLE 11

Instead of the 2% meta-benzophenone mono-sulfonyl chloride of Example 9, 2% meta-benzaldehyde monosulfonyl chloride with substantially the same results.

EXAMPLE 12

Into the "clear" vehicles of Examples 1, 7 and 8 there is incorporated 20% by weight of zinc oxide. The now "pigmented" vehicles are sensitized individually by 2% benzophenone sulfonyl chloride, acetophenone sulfonyl chloride and benzaldehyde sulfonyl chloride. Irradiated in the same manner as described in the foregoing examples the pigmented films cure to tack-free state at line speed of 100 feet per minute.

EXAMPLE 13

Into the "clear" vehicles of Examples 1, 7 and 8 there is incorporated 20% by weight of titanium dioxide (anatase). The pigmented vehicles are spread in 0.4 mil thick films on aluminum panels. Also reduced to comparably thin films are the pigmented vehicles in two parts. One has m-benzophenone sulfonyl chloride as a sensitizer.

On exposure to the apparatus described in Example 1 the only films to cure tack-free are those which contain the sensitizer of the invention; i.e., m-benzophenone sulfonyl chloride.

EXAMPLE 14

A polyester vehicle is prepared from 3 mol phthalic anhydride, 3 mol maleic anhydride, 6.8 mol propylene glycol and cooked to an acid number of about 30. Styrene is added until 70 n.v. (non-volatiles) is attained. Into the above "clear" polyester vehicle 2% by weight of paramethoxybutyrophenone sulfonyl chloride. Exposure of panels coated to 0.5 mil thick to irradiation at line speed of 100 feet per minute gives complete and tack-free cure.

EXAMPLE 15

A polyester vehicle is prepared from 3 mol maleic anhydride, 3 mol phthalic anhydride, 1 mol propylene glycol, and 6 mol propylene oxide and cooked to an acid number of about 30 after which hydroxyethylacrylate is added to constitute 50% by weight of the entire vehicle.

Into the above vehicle 2% by weight of meta-benzophenone sulfonyl chloride is incorporated, followed by applying the vehicle to test panels as earlier described. Subjecting the coated panels to the radiation emitted by the apparatus of Example 1, at line speed of 100 feet per minute produces tack-free, scratch resistant films. Without said sensitizer the film is wet and tacky even after repeated exposures to radiation.

EXAMPLE 16

A vehicle comprising tri-methylpropane tri-acrylate is sensitized with 2% of the reaction product formed by glycidyl acrylate and 2-carboxybenzophenone sulfonyl chloride. The films are applied to the test panels in about 0.5 mil thickness and are cured at 200 feet per minute as described hereinbefore to a tack-free state.

EXAMPLE 17

A vehicle comprising pentaerythritol tri-acrylate is sensitized by 2% para-methylbenzophenone sulfonyl chloride. Substantially the same excellent cure is obtained for 0.4 mil thick films at both line speeds of 100 and 200 feet per minute.

EXAMPLE 18

The same vehicle of Example 17 is sensitized with 2% bromomethylbenzophenone sulfonyl chloride with the results being substantially comparable when the same procedure is followed.

EXAMPLE 19

A "clear" vehicle is prepared from 1/2 phenylcellulose acrylate and 1/2 pentaerythritol triacrylate. 2% of meta-benzophenone monosulfonyl chloride is incorporated into said vehicle which is applied to a test panel as a film of about 1 mil thick. Following the irradiation procedure described in the preceding example the films cures to a tack-free state at a line speed of 100 feet per minute.

EXAMPLE 20

A vehicle is prepared from 1/3 pentaerythritol triacrylate, 1/3 2-diacrylate. Also incorporated into said vehicle is sufficient titania (rutile) to make up a paint with a pigment to vehicle ratio of 0.8 to 1.0. Into said paint is incorporated 2% by weight, based on vehicle, of meta-benzaldehyde monosulfonyl chloride and 0.3% by weight, based on the vehicle, of Michler ketone. The sensitized paint is applied in films of about 0.4 mil thick and irradiated in the same manner described earlier. The paint cures to a tack-free state at line speed of 100 feet per minute.

EXAMPLE 21

A "clear" vehicle is prepared from 1/3 pentaerythritol, 1/3 hydroxyethyl acrylate, and 1/3 ethyleneglycol diacrylate. 2% by weight of meta-benzophenone monosulfonyl chloride is incorporated into said clear vehicle dispersing well therein. The vehicle is applied in 0.4 mil film to a cardboard substrate, and then subjected to the apparatus described earlier at line speed of 200 feet per minute. The film show full and complete cure. The cardboard substrate

does not show any discoloration, distortion or degradation.

EXAMPLE 22

The vehicle described in Example 21 is prepared again to contain 3% by weight iron black (ferric oxide) making the now colored vehicle suitable as a printing ink. The colored vehicle is applied in a film of about 0.3 mil thick which is then subjected to the apparatus substrate described at 100 feet per minute. The cure is full and completed; no smudging is observed.

EXAMPLE 23

Into a vehicle comprising acrylated soybean oil (available commercially from Union Carbide Corporation, New York, N.Y. as Flexol Plasticizer EPO) is incorporated a 2% meta-benzophenone monosulfonyl chloride. The sensitized vehicle is applied to a heat sensitive plastics substrate (high density polyethylene) in a thin film of about 0.6 mil thick. The coated plastics substrate is then subjected to the curing procedure described above at 100 feet per minute. The coated film shows full cure and the substrate shows no distortion.

What is claimed is:

1. In a process for polymerizing an ethylenically unsaturated photopolymerizable vehicle in which a pigment is dispersed to form a pigmented composition, by exposure to U.V. radiation, the improvement which comprises incorporating into said vehicle about 0.5-5% by weight of a carbonylated phenyl nuclear sulfonyl chloride, said pigment being from about 20% to about 50% of said composition.

2. The process of claim 1 wherein said sulfonyl chloride is benzophenone sulfonyl chloride.

3. The process of claim 1 wherein said sulfonyl chloride is acetophenone sulfonyl chloride.

4. The process of claim 1 wherein said sulfonyl chloride is benaldehyde sulfonyl chloride.

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U.S. Cl. X.R.

96—115 P; 117—93.31, 142 R, 132 R, 138.8 R, 143 A; 204—159.14, 159.16, 159.18, 159.23; 260—2.5 B, 39 P, 39 M, 39 SB, 41 A, 41 B, 41 C, 41 AG, 77.5 CR, 80.75, 80.81, 86.1 E, 851, 856