

[54] **METHOD OF COATING RIGID CORES**

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[21] Appl. No.: **200,339**

Related U.S. Application Data

[63] Continuation of Ser. No. 879,175, Nov. 24, 1969, abandoned.

[52] U.S. Cl. **117/93.31**, 117/94, 117/161 UZ, 117/161 ZB, 204/159.15, 260/830 S

[51] Int. Cl. **B44d 1/50**, C08f 1/18, C08f 3/38

[58] Field of Search 117/93.31, 161 R, 117/161 UZ, 161 ZB, 94; 156/272, 446; 204/159.11, 159.22, 159.23, 159.15; 260/79, 830 S, 887, 874, 859

[56] **References Cited**

UNITED STATES PATENTS

1,182,982	5/1916	Crump	118/409
2,270,177	1/1942	Vawryk	118/409
3,361,842	1/1968	Applegath et al.	117/93.31
3,369,922	2/1968	Svrcek	117/94
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3,403,187	9/1968	Oswald et al.	117/93.31
3,697,302	10/1972	Ihara et al.	117/94

Primary Examiner—William D. Martin

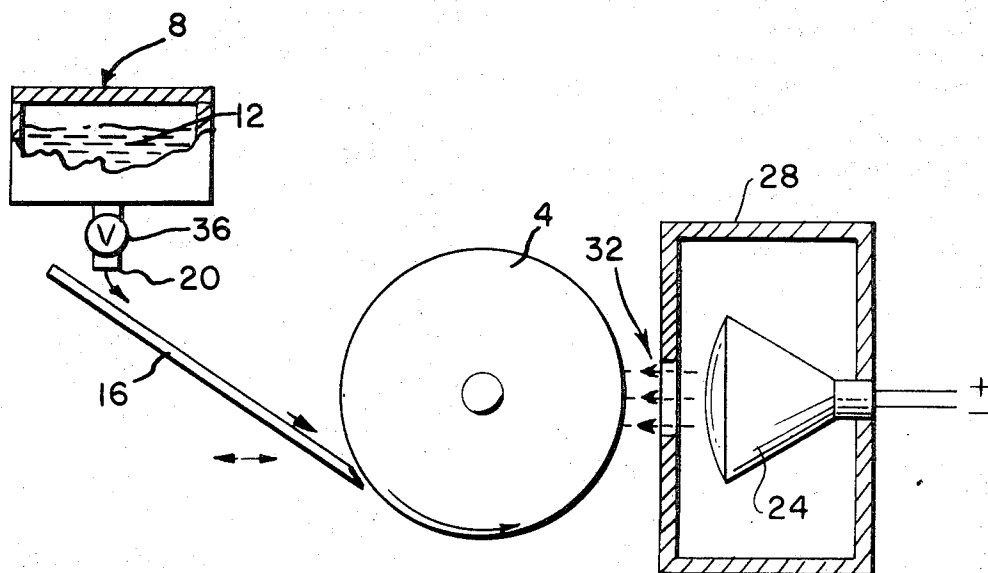
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[57] **ABSTRACT**

Industrial rollers are prepared by photocuring a layer of photocurable composition on the rigid core. As the core cylinder is rotated, a thin layer of photocurable composition is fed intermittently or continuously onto the rotating cylinder, where it can optionally be smoothed by a doctor blade. The photocurable composition preferably is photocured by an ultraviolet light source which is located on the cylinder side opposite the place where the photocurable composition is applied so that premature hardening does not occur in the feed stock. Multiple, consecutive layers of photocurable composition can be built up on the rigid core, each (after the first) being placed upon a partially hardened photocured sublayer. In this manner, the photocured material on the rigid core can be built up to any desired and practical thickness. The photocured surface of the roller can be ground and buffed to make a final product of accurately controlled dimensions.

16 Claims, 6 Drawing Figures



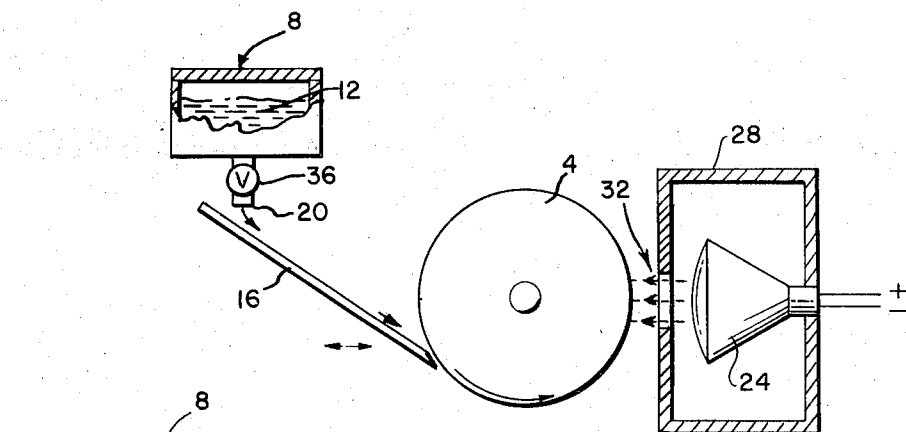


FIG. 1

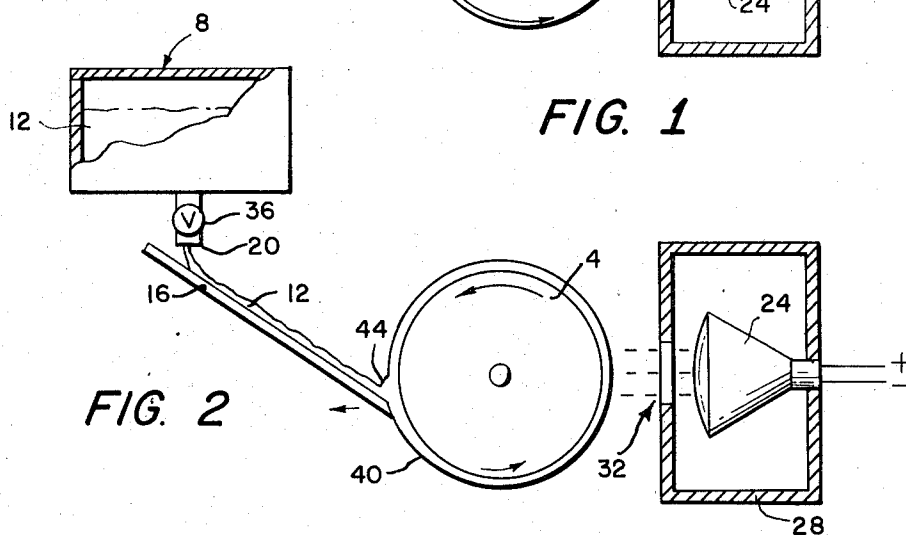


FIG. 2

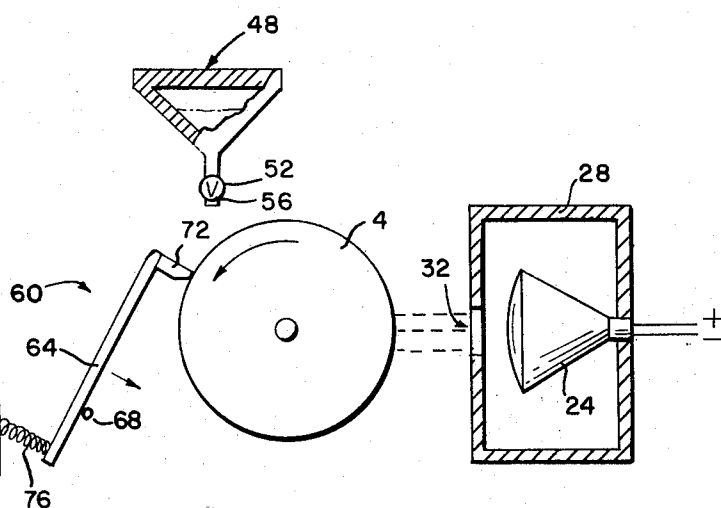


FIG. 3

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FIG. 4

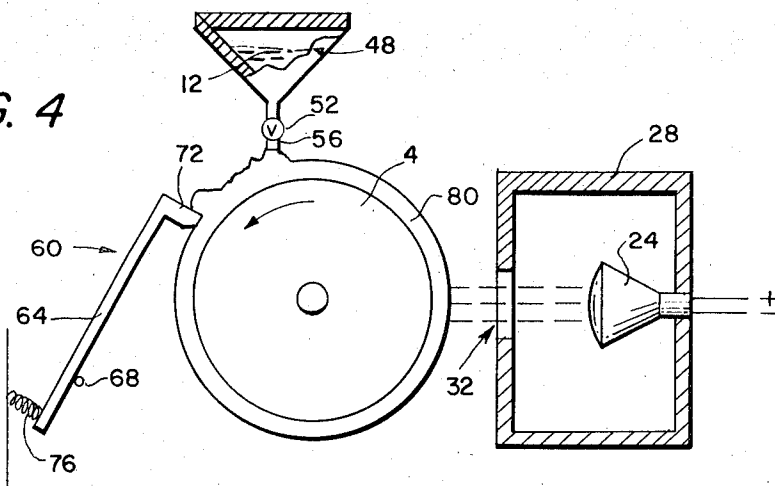


FIG. 5

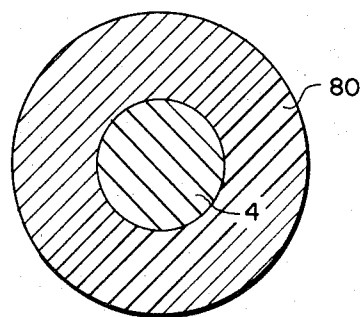
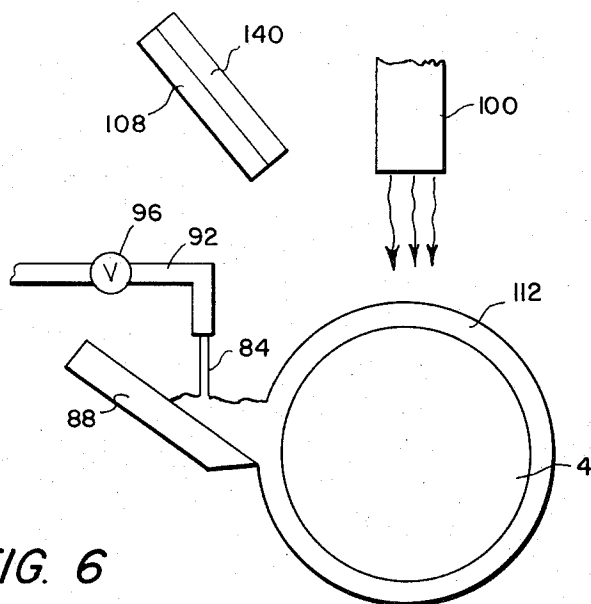


FIG. 6



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METHOD OF COATING RIGID CORES

This is a continuation, of application Ser. No. 879,175 filed 11-24-69, now abandoned.

BACKGROUND OF THE INVENTION

1. Objectives of the Invention

It is an object of this invention to prepare and apply coatings to rigid cores. Other objectives will be obvious to those skilled in the art.

2. Prior Art

A process is disclosed in U. S. Pat. No. 3,247,012 whereby a continuous coating is applied by brushing, dipping or spraying to an article in liquid form, and polymerized in situ by passing the coating and web under a beam of polymerization effecting electrons from an electron emitting means. A typical coating composition is a solution of an unsaturated polyester in a vinyl monomer, which upon copolymerization forms a cross-linked coating.

Typical means of dip coating a photosensitive layer, e.g., bichromated gelatin, onto a printing cylinder is given in U. S. Pat. No. 2,357,476. Another typical means of applying photosensitive layers, e.g., bichromated glue, grum, etc., onto a printing cylinder is given in U. S. Pat. No. 2,766,719. This means applies the layer in a conventional manner, but drying is required before imaging. In the above process, the photosensitive layer is exposed imagewise, the image is then developed reliefwise, and the nonimaged areas of the cylinder are etched. U. S. Pat. No. 3,304,909 describes a method for coating cylinders with urethanes which are subsequently subjected to a pressure roller and are cured by heating the entire apparatus contained in an oven for a substantial period of time after the cylinder has been coated to the desired thickness. This process has the disadvantage that the feed stock composition will also be cured thus causing long delays in cleaning up the apparatus after each roller coating operation.

Rubber coated rollers for various industrial applications are generally made by surrounding the cylindrical core with a liquid or solid elastomer in an appropriately-sized cylindrical mold. The mold is heated at elevated temperatures for long periods of time to vulcanize (or set) the rubber.

BROAD DESCRIPTION OF THE INVENTION

Industrial rollers are prepared by placing a layer of a photocurable composition on a revolving rigid core and photocuring the layer. The cylinder is rotated at a relatively slow rate of speed, i.e., between about 1 r.p.m. and the speed at which centrifugal force begins to distort the coating before it is photocured. A thin layer of photocurable composition is fed onto the rotating cylinder, where it can optionally be applied or smoothed by a doctor blade. Liquids of various viscosity ranges or thixotropic pastes are preferred but with suitable modifications of the feeding mechanism, semi-solid or "solid" resinous or elastomeric photocurable compositions can also be handled without departing from the scope of this invention; the main point is to select a photocurable composition which in the cured state will have the desired physical properties and solvent resistance for the intended application that the roller will be used for. During the application of the photocurable composition to the rotating core, the photocurable composition is intermittently or preferably continuously photocured by an ultraviolet light source. Prefer-

ably, the U. V. light source is located on the cylinder side opposite the place where the photocurable composition is applied so that premature hardening does not occur in the feed stock, which is maintained in the "shadow" cast by the core relative to the U.V. light source. Multiple consecutive layers of the same or different photocurable compositions can be placed on the rigid core, each (after the first) being located upon a partially or essentially completely hardened photocured sublayer. In this manner the photocured material on the rigid core can be built up to any desired and practical thickness, say, for example, 2 inches or more. Each layer, as it is applied, will normally be between about 0.5 and about 125 mils in thickness although this is not critical and may vary greatly depending on the speed of rotation of the core, the rate of retraction of the doctor blade or feeding from the applicator, the viscosity of the photocurable composition, and the curing rate of the photosensitive material. The photocured surface on the roller can, if desired, be ground and buffed to help make an end product having an extremely smooth surface and an accurate, e.g., cylindrical, shape.

An advantage of this invention is that expensive molds or long heating cycles are not needed to coat a rigid core. The process of this invention is quick, convenient and economical, and produces a superior, fully cured product, which usually has an extremely smooth, glaze-like surface. Post-fabrication curing or aging steps are not required, since the application and photocuring to completion (e.g., to constant final physical properties) of the photocurable composition is almost simultaneous and can be carried out under ambient conditions.

DETAILED DESCRIPTION OF THE INVENTION

The invention may be more clearly understood by reference to the following detailed description which is non-limiting but which merely exemplifies one of the preferred embodiments:

FIG. 1 is an end view, partially cross-sectional, of the apparatus before the coating process commences;

FIG. 2 is the same as FIG. 1 except that the coating process is in progress;

FIG. 3 is an end view, partially cross-sectional, of another embodiment of the apparatus before the coating process commences;

FIG. 4 is the same as FIG. 3 except that the coating process is in progress;

FIG. 5 is a transverse cross-sectional view of a coated and photocured roller; and

FIG. 6 is an end view, partially cross-sectional of another embodiment of this invention with the coating process in progress.

Referring to FIG. 1, roller core 4 rotates in a counter-clockwise direction. The mounting and moving means (not shown) for roller core 4 is any conventional device capable of rotating the core about its own axis (e.g., it is mounted on a lathe). Roller core 4 (1.5 in. dia. by 10 in.) can be cleaned before coating, and, in cases of metal rollers comprised of steel, can be sand-blasted prior to mounting to remove any rust and to expose a clean and slightly roughened coating surface. Adhesive bonding agents or primers may be applied if desired to impart good adhesion of the photocurable composition to the core surface. Reservoir 8, which may be heated if desired, contains photocurable composition 12.

(After photocurable composition 12 is prepared, it must be stored in a dark area, i.e., in the absence of ultraviolet light.) Delivery tray 16 is in a slightly sloping position, with the lower end (delivery lip) about 2 to 20 mils from the surface of roller core 4 during operation and start up (as shown in FIG. 2) and with the upper end (receiving portion) positioned under delivery throat 20 of reservoir 8. A plurality of delivery throats, etc., can be used to insure that there is coverage over the entire roller length. Photocurable composition 12 is gravity fed down delivery tray 16. Delivery tray 16 is moveable in a horizontal manner in relationship to roller core 4. Also delivery tray 16 has side walls (not shown) to prevent lateral overflow. U.V. light source 24 (e.g., one or several 275 watt RS sunlamps; is located so that its irradiating face is about 1.5 inches from the surface of roller core 4. Several sunlamps can be used, or a long tubular lamp could be used if desired. Shield 28 encompasses light source 24, except that slit 32 (0.75 in. by 5 in.) allows the ultraviolet light to be beamed directly onto the surface of roller core 4 without exposing photocurable composition 12 in delivery tray 16.

In operation, roller core 4 is typically rotating at about 10 r.p.m. Valve 36 is opened in such a manner as to properly control the amount of photocurable composition 12 flowing down delivery tray 16. Light source 24 is activated. As photocurable composition 12 contacts the surface of rotating roller core 4, it adheres thereto as a layer (i.e., coating 40 as in FIG. 2). It is seen that since the direction of rotation of roller core 4 is counterclockwise, the lip delivery tray 16 serves as a doctor blade to control the thickness of the applied coating on each pass. During the coating operation, "rolling bank" 44 of viscous photocurable composition 12 is preferably maintained in the end of delivery tray 16 against the surface of core 4. As the uncured coating passes U. V. light source 24, it is photocured. The coating thickness can be increased by applying another coating of uncured photocurable composition 12 on photocured composition 12 by moving the edge of delivery tray 16 slowly away from coated roller core 4. Coating thicknesses as great as about 2.0 or more inches can be obtained, and customary total thicknesses up to about 0.5 - 1.0 inch are easily obtained. After achieving the desired coating thickness, delivery tray 16 is retracted away from the coated surface of roller core 4. The roller is rotated for several seconds to several minutes thereafter to insure a complete photocure of the coating of photocurable composition 12. The coatings are essentially non-tacky and are usually applied in less than about 15-30 minutes of total operating time, depending on the ultimate coating thickness, the intensity of the light source, etc.

Referring to FIG. 3, a different embodiment of this invention is shown. Roller core 4 and the light source arrangement are the same as in FIG. 1. Reservoir 48 (which may be heated if desired) contains photocurable composition 12, which is dropped onto the top of roller core 4 by means of delivery throat 52 during operation and start up (as shown in FIG. 4). The flow rate is controlled by means of valve 56. Scraper 60 consists of arm 64, which is pivoted at 68, and scraper blade 72. Arm 64, on the other side of pivot 68 from blade 72, is attached to tension spring 76, which keeps the tip of blade 72 firmly pressed against roller 4 as it rotates counterclockwise.

In operation, as best shown in FIG. 4, valve 52 is opened and photocurable composition flows onto rotating roller 4. Blade 72 forces photocurable composition 12 into a smooth layer. Photocurable composition 12 is viscous enough to remain in a thin, even layer until it is photocured by U.V. light source 24. As roller core 4 continues to rotate, the thickness of photocured layer 80 builds up. FIG. 5 shows a finished roller (roller core 4 and photocured composition 80) which has been ground and buffed.

The core is typically constructed of a metal, e.g., aluminum, copper, steel, etc., but also can be constructed of a non-metallic substance. The core can be a solid cylinder, a porous sintered cylinder, a hollow pipe or tube, a porous polymeric structure, etc. An example of a porous structure is a filament wound spindle. Because of the low temperature and pressure used during the photocuring step, the core can be made from materials which cannot withstand the prolonged heating used with heat curable roller coatings such as those derived from wood, cardboard, synthetic plastics, fiber-reinforced composites, foamed resins or elastomers, etc.

The method of applying the photocurable composition to the roller core (cylinder) is not critical, and can also, typically, be a forced-feed mechanism such as the use of a roller transfer to the core, an extrusion transfer, a curtain coating or knife coating, etc. Also a dip coating or spray coating technique can be used when the photocurable composition is of a relatively low viscosity.

The photocuring means is an actinic radiation source. It can be an ultraviolet radiation source that is composed of one or more individual U.V. sources, e.g., a sun lamp, mercury vapor lamp, carbon arc, pulsed xenon arc, etc., several batteries of individual sources, and so forth. Other actinic electromagnetic or actinic ionizing radiation sources can be used, e.g., electron beams, gamma rays, lasers, visible radiation sources, infrared radiation sources, etc., if the coating composition is formulated properly so that satisfactory rates of curing can be attained therewith and if the radiation can be so directed, focussed or collimated by shielding and the like so as to photocure the coating on the core but not the feed stream, etc.

The coating substance is preferably a photocurable composition, and particularly those having elastomeric properties, and particularly those having elastomeric properties in the photocured state. However, photopolymerizable compositions and photocrosslinkable compositions may be used if the end properties are suitable for the intended roller application. As broadly used in this application, the term "photocurable" includes those curing mechanisms which are initiated by actinic electromagnetic and/or actinic ionizing radiation sources, e.g., ultraviolet, visible, infrared radiation, electron beams, gamma rays, lasers, etc. Combinations of the above forms of radiation also can be used if so desired to obtain special process advantages, and, as a matter of fact, common U.V. light sources emit visible and infrared radiation simultaneously.

Referring to FIG. 6, a different embodiment of this invention is shown. Roller core 4 is the same as in FIG. 1. The photocurable composition 76 (optionally without any photocuring rate accelerator) is in a reservoir (not shown) and is delivered to the top of doctor blade 88 via feed line 92. Doctor blade 88 is slightly tipped

and is similar to delivery tray 16 in FIG. 1. The flow rate of composition 16 is controlled by means of valve 96. Electron beam source 100 is located above rotating core 4. Radiation shield 104 is positioned as shown in FIG. 6. Mirror 108, on the back of radiation shield 104, aids the operator in seeing the coating operation.

The operation shown in FIG. 6 is the same as shown in FIG. 1 and 2 except that the photocuring is achieved (operating by remote controls) by means of electron beam source 100. The resultant roller includes core 4 and photocured layer 112.

The crucial ingredients in the preferred photocurable composition are:

1. about 2 to about 98 parts by weight of an ethylenically unsaturated polyene (or polyyne) containing two or more reactive unsaturated carbon-to-carbon bonds;
2. about 98 to about 2 parts by weight of a polythiol; and
3. about 0.0005 to about 50 parts by weight (based on 100 parts by weight of (1) and (2) of a photocuring rate accelerator.

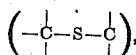
It is to be understood, however, that when energy sources other than visible or ultraviolet light are used to initiate the curing reaction, photocuring rate accelerators (i.e., photosensitizers, etc.) generally are not required in the formulation. That is to say, the actual composition of the photocuring rate accelerator, if required, may vary with the type of energy source that is used to initiate the curing reaction.

The reactive carbon-to-carbon bonds of the polyenes are preferably located terminally, near terminally, and/or pendant from the main chain. The polythiols, preferably, contain two or more thiol groups per molecule. The photocurable compositions are liquid (i.e., flowable) over the temperature range provided during the application to the rotating core.

Included in the term "liquid," as used herein, are those photocurable compositions which in the presence of inert solvent, aqueous dispersion or plasticizer have a viscosity ranging from slightly above zero to 20 million centipoises at 130°C. The term "liquids" includes suspensions, etc.

As used herein polyenes and polynes refer to simple or complex species of alkenes or alkynes having a multiplicity, i.e., at least 2, "reactive" carbon-to-carbon unsaturated functional groups per average molecule. For example, a diene is a polyene that has two "reactive" carbon-to-carbon double bonds per average molecule, while a diyne is a polyyne that contains in its structure two "reactive" carbon-to-carbon triple bonds per average molecule. Combinations of "reactive" carbon-to-carbon triple bonds within the same molecule are also operable. An example of this is monovinylacetylene, which is a polyeneyne under our definition. For purposes of brevity all these classes of compounds will be referred to herein as polyenes.

As used herein the term "reactive" unsaturated carbon-to-carbon groups means groups which will react under proper conditions as set forth herein with thiol groups to yield the thioether linkage



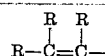
as contrasted to the term "unreactive" carbon-to-carbon unsaturation which means



groups when found in aromatic nuclei (cyclic structures exemplified by benzene, pyridine, anthracene, and the like) which do not under the same conditions react with the thiols to give thioether linkages. In the instant invention products from the reaction of polyenes with polythiols which contain 2 or more thiol groups per average molecule are called polythioether polymers or polythioethers.

Methods of preparing various polyenes, with the limitations set forth herein, useful within the scope of this invention are disclosed in copending application Ser. No. 674,773, filed Oct. 12, 1967, now abandoned, and assigned to the same assignee. Some of the useful polyenes are prepared in the detailed examples set forth in the following specification. The general formulas for several, useful, representative polyenes and polynes are given in the Figure in Dutch (Holland) Application No. 67/10439 which was laid open to public inspection and copying thereof on Jan. 29, 1968 (said pertinent portions of said public document being incorporated herein by reference).

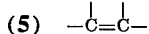
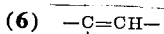
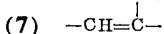
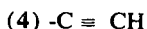
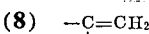
One group of polyenes, with the limitations set forth herein, operable in the instant invention is that taught in a copending application having Ser. No. 617,801, inventors: Kehr and Wszolek, filed: Feb. 23, 1967, now abandoned and assigned to the same assignee. This group includes those having a molecular weight in the range of 50 to 20,000, a viscosity ranging from 0 to 20 million centipoises at 70°C. of the general formula: $[A]-(X)_m$, wherein X is a member of the group consisting of



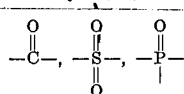
and $R-C \equiv C-$; m is at least 2; R is independently selected from the group consisting of hydrogen, halogen, and an organic compound selected from the group consisting of aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, aralkyl, substituted aralkyl, alkyl and substituted alkyl groups containing one to four carbon atoms; and A is a polyvalent organic moiety free of (1) reactive carbon-to-carbon unsaturation and (2) unsaturated groups in conjugation with the reactive ene or yne groups in X . Thus A may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P or O but contains primarily carbon-carbon, carbon-oxygen or silicon-oxygen containing chain linkages without any reactive carbon-to-carbon unsaturation. This group preferably has a molecular weight over 300.

In this first group, the polyenes are simple or complex species of alkenes or alkynes having a multiplicity of pendant, terminally or near terminally positioned "reactive" carbon-to-carbon unsaturated functional groups per average molecule. As used herein for determining the position of the reactive functional carbon-to-carbon unsaturation, the term "terminal" means that said functional unsaturation is at an end of the main chain in the molecule; whereas by "near terminal" is meant that the functional unsaturation is not more than four carbon atoms away from an end of the main chain in the molecule. The term "pendant" means that the reactive carbon-to-carbon unsaturation is located terminally or near terminally in a branch of the main chain as contrasted to a position at or near the ends of the main chain. For purposes of brevity all of these positions will be referred to generally as "terminal" unsaturation.

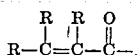
The liquid polyenes operable in this first group contain one or more of the following types of non-aromatic and non-conjugated "reactive" carbon-to-carbon unsaturation:



These functional groups as shown in 1-8 supra are situated in a position either which is pendant, terminal or near terminal with respect to the main chain but are free of terminal conjugation. As used herein the phrase "free of terminal conjugation" means that the terminal "reactive" unsaturated groupings may not be linked directly to non-reactive species, such as



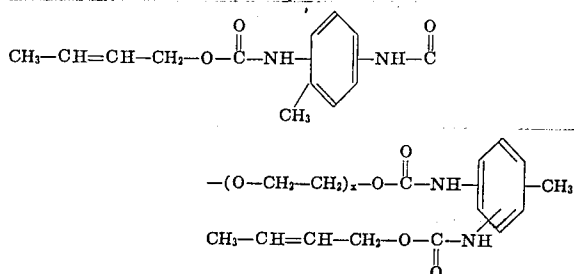
and the like, so as to form a conjugated system of unsaturated bonds exemplified by the structure:



etc. On the average the polyenes must contain 2 or more "reactive" unsaturated carbon-to-carbon bonds per molecule and have a viscosity in the range from slightly above 0 to about 20 million centipoises at 70°C. Included in the term "polyenes" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the viscosity range set out above at 70°C. Operable polyenes in the instant invention have molecular weights in the range of about 50 to about 20,000, preferably about 500 to about 10,000.

Examples of operable polyenes from this first group include, but are not limited to:

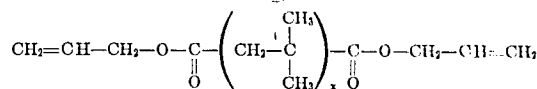
1. Crotyl-terminated polyurethanes which contain two "reactive" double bonds per average molecule in a near terminal position of the average general formula:



wherein x is at least 1.

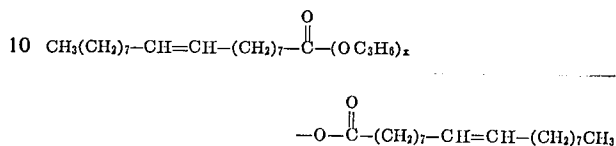
2. Ethylene/propylene/non-conjugated diene terpolymers, such as Nordel 1040° manufactured by E. I. du Pont de Nemours & Co., Inc., which contains pendant "reactive" double bonds of the formula: $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$

3. The following structure which contains terminal "reactive" double bonds:



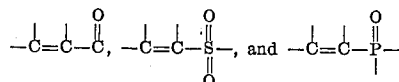
5 wherein x is at least 1.

4. The following structure which contains near terminal "reactive" double bonds:



15 wherein x is at least 1.

A second group of polyenes operable in this invention includes those polyenes in which the reactive unsaturated carbon-to-carbon bonds are conjugated with adjacent unsaturated groupings. Examples of operable conjugated reactive ene systems include but are not limited to the following:



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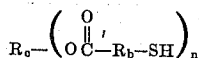
A few typical examples of polymeric polyenes which contain conjugated reactive double bond groupings such as those described above are poly(oxyethylene) glycol (600 M.W.) diacrylate; poly(oxytetramethylene) glycol (1,000 M.W.) dimethacrylate; the triacrylate of the reaction product of trimethylol propane with 20 moles of ethylene oxide; and the like.

As used herein, the term polythiols refers to simple or complex organic compounds having a multiplicity of pendant or terminally positioned $-\text{SH}$ functional groups per average molecule.

On the average the polythiols must contain 2 or more $-\text{SH}$ groups per molecule. They usually have a viscosity range of slightly above 0 to about 20 million centipoises (cps) at 70°C., as measured by a Brookfield Viscometer. Included in the term "polythiols" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the viscosity range set out above 70°C. Operable polythiols in the instant invention usually have molecular weights in the range about 50 to about 20,000, or more, preferably about 100 to about 10,000.

The polythiols operable in the instant invention can be exemplified by the general formula: $\text{R}_a-(\text{SH})_n$, wherein n is at least 2 and R_a is a polyvalent organic moiety free from "reactive" carbon-to-carbon unsaturation. Thus R_a may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P or O but primarily contains carbon-hydrogen, carbon-oxygen, or silicon-oxygen containing chain linkages free of any "reactive" carbon-to-carbon unsaturation.

One class of polythiols operable with polyenes in the instant invention to obtain essentially odorless compositions are esters of thiol-containing acids of the general formula: $\text{HS}-\text{R}_b-\text{COOH}$, wherein R_b is an organic moiety containing no "reactive" carbon-to-carbon unsaturation with polyhydroxy compounds of the general structure: $\text{R}_c-(\text{OH})_n$ wherein R_c is an organic moiety containing no "reactive" carbon-to-carbon unsaturation and n is 2 or greater. These components will react under suitable conditions to give a polythiol having the general structure:



wherein R_b and R_c are organic moieties containing no "reactive" carbon-to-carbon unsaturation and n is 2 or more.

Certain polythiols, such as the aliphatic monomeric polythiols (ethane dithiol, hexamethylene dithiol, dodecamethylene dithiol, tolylene-2,4-dithiol, etc.), some polymeric polythiols, such as a thiol-terminated ethylcyclohexyl dimercaptan polymer, etc., and similar polythiols which are conveniently and ordinarily synthesized on a commercial basis, although having obnoxious odors, are operable in this invention. Examples of the polythiol compounds preferred for this invention because of their relatively low odor level and fast curing rate include but are not limited to esters of thioglycolic acid ($HS-CH_2COOH$), α -mercaptopropionic acid ($HS-CH(CH_3)-COOH$) and β -mercaptopropionic acid ($HS-CH_2CH_2COOH$) with polyhydroxy compounds such as glycols, triols, tetraols, pentaols, hexaols, etc. Specific examples of the preferred polythiols include but are not limited to ethylene glycol bis(thioglycolate), ethylene glycol bis(β -mercaptopropionate), trimethylolpropane tris(thioglycolate), trimethylolpropane tris(β -mercaptopropionate), pentaerythritol tetrakis(thioglycolate) and pentaerythritol tetrakis(β -mercaptopropionate), all of which are commercially available. A specific example of a preferred polymeric polythiol is poly(propylene ether) glycol bis(β -mercaptopropionate) which is prepared from poly(propylene ether) glycol (e.g., Pluracol P2010, Wyandotte Chemical Corp.) and β -mercaptopropionic acid by esterification.

The preferred polythiol compounds are characterized by a low level of mercaptan-like odor initially, and after reaction give essentially odorless cured polythioether end products which are commercially useful resins or elastomers for roller coatings.

As used herein the term "odorless" means the substantial absence of the well-known offensive and sometimes obnoxious odors that are characteristic of hydrogen sulfide and the derivative family of compounds known as mercaptans.

The term "functionality" as used herein refers to the average number of ene or thiol groups per molecule in the polyene and/or the polythiol. For example, a triene is a polyene with an average of three "reactive" carbon-to-carbon unsaturated groups per molecule and thus has a functionality of 3. A dithiol is a polythiol with an average of two thiol groups per molecule and thus has a functionality of 2.

It is further understood and implied in the above definitions that in these systems the functionality of the polyene and the polythiol component is commonly expressed in whole numbers although in practice the actual functionality may be fractional. For example, a polyene component having a nominal functionality of 2 (from theoretical considerations alone) may in fact have an effective functionality of somewhat less than 2. Such a product is useful in the instant invention and is referred to herein as having a functionality of 2.

To obtain the maximum strength, solvent resistance, creep resistance, heat resistance and freedom from tackiness, the reaction components consisting of the polyenes and polythiols of this invention generally are formulated in such a manner as to give solid, cross-

linked, three dimensional network polythioether polymer systems or curing. In order to achieve such infinite network formation, the individual polyenes and polythiols must each have a functionality of at least 2 and the sum of the functionalities of the polyene and polythiol components must always be greater than 4. Blends and mixtures of the polyenes and the polythiols containing said functionality are also operable herein.

The preferred photocuring reaction can be initiated by U.V. radiation contained in actinic radiation from sunlight or obtained from special light sources which emit significant amounts of U.V. light. (Useful U.V. radiation generally has a wavelength in the range of about 2,000 to about 4,000 angstrom units.) Thus it is possible merely to expose the polyene and polythiol admixture to actinic radiation under ambient conditions or otherwise and obtain a cured solid elastomeric or resinous product useful as a core coating material. But this approach to the problem results in extremely long exposure times which cause the process in the vast bulk of applications to be commercially unfeasible. Chemical photocuring rate accelerators (photoinitiators or photosensitizers or photoactivators) e.g., quinone, methyl ethyl ketone, etc., serve to drastically reduce the exposure time and thereby when used in conjunction with various forms of energetic radiation (containing U.V. radiation) yield very rapid, commercially practical photocures by the practice of the instant invention. Useful photocuring rate accelerators include benzophenone; acetophenone; acenaphthene-quinone; methyl ethyl ketone; thioxanthene-9-one; xanthene-9-one; 7-H-Benz [de] anthracene-7-one; dibenzosuberone; 1-naphthaldehyde; 4,4'-bis(dimethylamino) benzophenone; fluorene-9-one; 1'-acetonaphthone; 2'-acetonaphthone; 2,3-butanedione; anthraquinone; 1-indanone; 2-tert-butyl anthraquinone; valerophenone; hexanophenone; 8-phenylbutyrophene; p-morpholinopropiophenone; 4-morpholinobenzophenone; 4'-morpholinodesoxybenzoin; p-diacetylbenzene; 4-aminobenzophenone; 4'-methoxyacetophenone; benzaldehyde; α -tetralone; 9-acetylphenanthrene; 2-acetylphenanthrene; 10-thioxanthene; 3-acetylphenanthrene; 3-acetylindole; 1,3,5-triacetylbenzene; etc.; and blends thereof. The photoinitiators are added in an amount ranging from about 0.0005 to about 50 percent by weight of the polyene and polythiol components in the instant invention. Benzophenone is the preferred photocuring rate accelerator.

The compositions to be photocured, i.e., converted to roller core coatings, in accord with the present invention may, if desired, include such additives as antioxidants, inhibitors, activators, fillers, pigments, dyes, antistatic agents, flame-retardant agents, thickeners, thixotropic agents, surface-active agents, viscosity modifiers, plasticizers, and the like within the scope of this invention. Such additives generally are preblended with the polyene or polythiol prior to impregnating it in and/or on the ultimate structure. The aforesaid additives may be present in quantities up to 500 parts or more per 100 parts photocurable composition by weight and preferably 0.0005 to 300 parts on the same basis. The type and concentration of the additives must be selected with great care so that the final composition remains photocurable under conditions of exposure.

The compounding of the components prior to photocuring can be carried out in any conventional manner which takes into account that the material is sensitive

to U.V. radiation. This composition generally can be stored in the dark for extended periods of time prior to actual use or even incorporation in and/or on the ultimate structure.

It is often desirable to place a suitable anti-oxidant, e.g., "Ionol", hydroquinone, *t*-butyl catechol, etc., in the photocurable composition. These agents in optimum amounts will help to stabilize the fully formulated composition against premature thickening or curing during periods of storage prior to use in the coating process.

The following examples will aid in explaining, but should not be deemed as limiting, the instant invention. In all cases, unless otherwise noted, all parts and percentages are by weight.

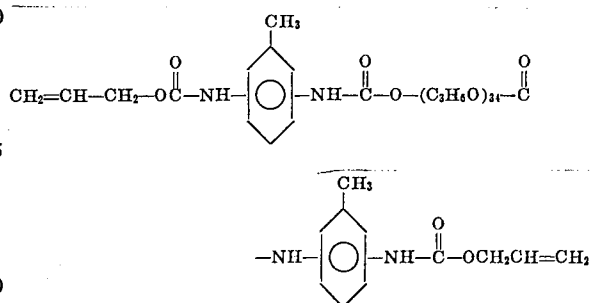
EXAMPLE 1

3456.3 gm. (1.75 mole) of poly(propylene ether) glycol, commercially available under the trade name "PPG 2025" from Union Carbide, and 1.7 gm. of di-*n*-butyl tin dilaurate were placed in a 5-liter, round-bottom, 3-neck flask. The mixture in the flask was degassed at 110°C. for one hour and was then cooled to 25°C. by means of an external water bath. 207 gm. (3.50 moles) of allyl alcohol, with stirring, were added to the flask. 609.0 gm (3.50 moles) of an 80 to 20 percent isomer mixture of tolylene-2,4-diisocyanate and tolylene-2,6-diisocyanate, respectively, sold under the trade name "Mondur TD 80," was charged to the flask. The mixture was stirred well. The flask was cooled by the water bath during this period. Eight minutes after the "Mondur TD 80" was added, the temperature of the mixture was 59°C. After 20 minutes, the NCO content was 12.39 mg. NCO/gm.; after 45 minutes, it was 9.87 mg. NCO/gm.; and after 75 minutes, it was 6.72 mg. NCO/gm. The water bath was removed 80 minutes after the "Mondur TD 80" had been added, the temperature of the mixture being 41°C., and heat was applied until the mixture temperature reached 60°C. That temperature was maintained. 105 minutes after the "Mondur TD 80" was added, the NCO content was 3.58 mg. NCO/gm.; after 135 minutes, it was 1.13 mg. NCO/gm.; and after 195 minutes, it was 0.42 mg. NCO/gm. At that point in time, the resultant polymer composition was heated to 70°C., and vacuum-stripped for 1 hour. The resultant polymer composition was labeled composition 1, and had a viscosity of 16,000 cps. as measured on a Brookfield Viscometer at 30°C. Unless otherwise stated, all the viscosity measurements were made on a Brookfield Viscometer at 30°C.

The above procedure was repeated five times, and resultant compositions were labeled compositions 2 to 6, respectively. The heating step lasted 180 minutes, 140 minutes, 205 minutes and 180 minutes, respectively. With composition 2, the temperature was 60°C. after 8 minutes; with composition 3, the temperature was 57°C. after 6 minutes; with composition 4, the temperature was 41°C. after 20 minutes, at which time the temperature was raised and held at 60°C.; with composition 5, the temperature was 57.5°C. in 8 minutes, was 42°C. in 40 minutes, then taken up to 60°C. and lowered to 58°C. after 120 minutes; and with composition 6, the temperature was 57°C. in 6 minutes, and was 41°C. after 60 minutes, at which time the temperature was immediately raised to 60°C. The viscosity of the resultant polymer compositions was 15,500 cps.; 16,000

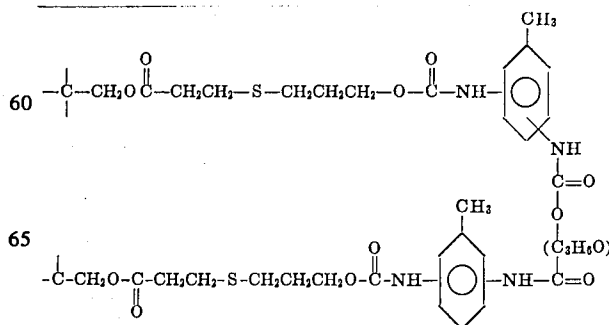
cps.; 17,000 cps.; 16,800 cps.; and 16,200 cps. respectively.

Compositions 1,2,3,4,5, and 6 were placed in a 6-gallon container and stirred well. The resultant polymer composition had a viscosity of 16,000 cps. and the NCO content was 0.01 mg. NCO/gm. This composite polymer composition was labeled polymer A, which has the following approximate structure:



100 parts of polymer A, 10 parts of polythiol A, 1.5 parts of benzophenone and 0.1 part by weight of "Ionol" were thoroughly admixed. This resulted in photocurable composition A. Polythiol A was pentaerythritol tetrakis(β-mercaptopropionate), which is commercially available under the trade name "Q-43 Ester" (sold by Carlisle Chemical Company). "Ionol" is a table designation for 2,6-di-*tert*-butyl-4-methylphenol (sterically hindered) and is commercially available from Shell Chemical Company. Ionol has good anti-oxidant properties, is nonirritating to the skin, and has a comparatively inert, non-acidic hydroxyl group.

Photocurable composition A was placed in a reservoir like the one shown in FIG. 1. The rest of the experiment was similar to that shown in FIG. 1 and the accompanying write-up above. The end of the delivery tray was placed about 20 mils away from the roller core (steel). The roller core was rotated at 25 r.p.m. The valve on the throat of the reservoir was opened. As the coating was applied to the roller core, the delivery tray was slowly moved (manually) away from the core. When the coating thickness reached about one-fourth inch, the delivery tray was completely backed away from the coated roller. The coated roller was further rotated for 3 minutes before the U.V. lamp was turned off. The resultant photocured coating was smooth and had a glaze-like finish. The final hardness of the coating was measured at Shore A 30 (ASTM). A typical segment of the three dimensional crosslinked, polythioether product is:



EXAMPLE 2

Example 1 was repeated except that 15 parts of polythiol A was used. The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 3 to 6

Example 1 was repeated four times, except that the pentaerythritol tetrakis (β -mercaptopropionate) was replaced with trimethylolpropane tris (β -mercaptopropionate) (10 parts) (Example 3), trimethylolpropane tris(thioglycolate) (15 parts) (Example 4), pentaerythritol tetrakis (thioglycolate) (5.0 parts) (Example 5), poly(propylene-ether)triol tris (β -mercaptopropionate) of M.W. 3400 (100 parts) (Example 6), respectively. The resultant photocured coatings were smooth and had a glaze-like finish.

EXAMPLE 7

Example 1 was repeated, except that half of the pentaerythritol tetrakis (β -mercaptopropionate) was replaced with 5 parts of ethylene glycol bis(β -mercaptopropionate). The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 8

Example 1 was repeated except that 60 parts of polymer C was used in place of polymer A. Polymer C was prepared as follows: 458 gm. (0.23 mole) of a commercially available liquid polymeric diisocyanate sold under the trade name Adiprene L-100° by E. I. duPont de Nemours & Co. was charged to a dry resin kettle maintained under a nitrogen atmosphere and equipped with a condenser, stirrer, thermometer, and gas inlet and outlet. 37.8 gm. (0.65 mole) of allyl alcohol was charged to the kettle and the reaction was continued for 17 hours with stirring at 100°C. Thereafter the nitrogen atmosphere was removed and the kettle was evacuated 8 hours at 100°C. 50 cc. dry benzene was added to the kettle and the reaction product was azeotroped with benzene to remove the unreacted alcohol. This allyl-terminated liquid polymer had a molecular weight of approximately 2100 and was labeled polymer C.

The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 9

Example 1 was repeated except that 100 parts of polymer D was used in place of polymer A. Polymer D was prepared as follows: 1,500 gm. (0.47 mole) of a linear solid polyester diol having a molecular weight of 3,200 and commercially available from Hooker Chemical Corp. under the trade name "Rucoflex S-1011-35" was charged to a 3-liter, 3-necked flask and heated to 110°C. under vacuum and nitrogen for 1 hour with stirring. 83 gm. of allyl isocyanate having a molecular weight of 83.1 and commercially available from Upjohn Co. was added to the flask along with 0.3 cc. of dibutyl tin dilaurate (catalyst), commercially available from J. T. Baker Co. The reaction was continued at 110°C. with stirring for 1 hour. This allyl-terminated polymer was labeled polymer D.

The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 10 to 15

Example 1 was repeated six times, except that the benzophenone was replaced with cyclohexanone (2.0 parts) (Example 10), acetone (1 part) (Example 11), acetophenone (0.3 part) (Example 12), dibenzosuberone (0.5 part) (Example 13), a blend of acetone (0.3 part) and p-diacetylbenzene (0.6 part) (Example 14), and 3-acetylphenanthrene (1 part) (Example 15), respectively. The resultant photocured coatings were smooth and had glaze-like finishes.

EXAMPLES 16

Example 1 was repeated twice, except that the roller core was constructed of copper (Example 16) and fiberglass reinforced polyester resin (Example 17), respectively. The resultant photocured coatings were smooth and had a glaze-like finish.

Example 18

This example illustrates the use of a monomeric polythiol and a monomeric polyene. 23.8 gm. of pentaerythritol tetrakis(β -mercaptopropionate); 25.6 gm. of the reaction product of one mole of 1,4-butanediol with two moles of allyl isocyanate; and 0.5 gm. of benzophenone were thoroughly admixed. Example 1 was repeated, except that the above photocurable composition was used in place of photocurable composition A. The resultant photocured coating was smooth, hard and had a glaze-like finish.

EXAMPLE 19

This example illustrates the use of a reactive ene group conjugated with another double bond grouping ($C=O$). 27 gm. of the triacrylate of the reaction product of one mole of trimethylol propane with 20 moles of ethylene oxide; 9 gm. of pentaerythritol tetrakis(β -mercaptopropionate); and 0.5 gm. of benzophenone were thoroughly admixed. Example 1 was repeated, except that the above photocurable composition was used in place of photocurable composition A. The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 20

This example illustrates the use of photocurable composition containing a monomeric polyene and a polymeric polythiol. 50 gm. of "Dion Polymercaptan Resin DPM-1002," which is a thiol terminated liquid polymer having a functionality of 2 to 3 and a molecular weight of about 5000 and commercially available from Diamond Alkali Company; 2.5 gm. of triallyl cyanurate; and 0.5 gm. of benzophenone were admixed. Example 1 was repeated, except that the above photocurable composition was used in place of photocurable composition A. The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 21

This example illustrates the use of a photocurable composition containing a polymeric polyene and a polymeric polythiol. Example 1 was repeated, except that the photocurable composition contained 50 parts of the polymeric polyene used in Example 8; 100 parts of the polymeric polythiol used in Example 20; and 0.5 part of benzophenone. The resultant photocured coating was smooth and had a glaze-like finish.

EXAMPLE 22

Photocurable composition A was placed in a reservoir like the one shown in FIG. 3. The rest of the experimental set-up was similar to that shown in FIG. 3 and the accompanying write-up above about the set-up in FIG. 3. The roller core (one in. dia.) was rotated at 15 r.p.m. The valve on the throat of the reservoir was opened. When the coating thickness reached a little over one inch, the flow of the photocurable composition was completely turned off. Blade 72 was backed away from roller 4. The coated roller was further rotated for 3 minutes before the U.V. lamp was turned off. The resultant photocured coating was smooth and had a glaze-like finish, but was ground and buffed to supply a matte surface.

EXAMPLE 23

Photocurable composition X was prepared by admixing 100 parts of polymer A, 10 parts of polythiol A and 0.1 part of "Ionol." Photocurable composition X was placed in a reservoir and fed to doctor knife 4 via feed line 92 as shown in FIG. 6. Photocurable composition X was coated on rotating core 4. Doctor blade 88 was retracted at a rate of 0.01 inch per revolution of roller core 4. Roller core 4 (a 4 inch diameter steel roller) was rotated at 10 r.p.m. Electron beam source — was tuned on as the coating started. Electron beam source — was a 500 kw insulated core transformer commercially available from High Voltage Engineering Co. After the coating and irradiation had proceeded for 5 minutes, the feed of photocurable composition X was stopped. After the photocurable composition X in the bank of the doctor rod — had been consumed, as observed through mirror — the electron beam irradiation was continued for 1 minute to assure complete cure of surface layer — of the roller. When roller — was removed it was found that coated photocurable composition X was cured to an elastomer and that the surface was smooth. The roller was ground to a 5.00 inch O.D. roller of good quality.

It is claimed:

1. A process for preparing a coated cylindrical core which comprises:

- a. admixing a photocurable composition consisting essentially of about 2-98 parts by weight of an ethylenically unsaturated polyene containing 2 or more reactive unsaturated carbon to carbon bonds per molecule, about 98 to about 2 parts by weight of polythiol containing 2 or more thiol groups per molecule, the total combined functionality of the reactive unsaturated carbon to carbon bonds per molecule in the polyene and the thiol groups per molecule in the polythiol being greater than 4, and about 0.0005 to about 50 parts by weight based on 100 parts by weight of the polyene and polythiol of a photocuring rate accelerator;
- b. applying said photocurable composition uniformly to the surface on a line parallel to the longitudinal axis of a rotating cylindrical core to gradually build up layer by layer a coating on said core; and
- c. curing said photocurable composition coating on said rotating cylindrical core, whereby said curing is achieved by subjecting said photocurable composition to actinic or electron beam radiation.

2. A process as described in claim 1 wherein said photocuring is achieved by means of ultraviolet radiation.

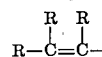
3. A process as described in claim 1 wherein said photocuring is achieved by means of electron beam radiation.

4. A process as described in claim 1 wherein said coating and said photocuring occur simultaneously, said photocuring occurring in the freshly coated layer and in previously coated layers present.

5. A process as described in claim 1 wherein said photocurable composition comprises an ethylenically unsaturated polyene having at least two reactive ene groups per molecule, a polythiol containing two or more thiol groups per molecule, and a photocuring rate accelerator, where the sum of the functionalities of said polyene and said polythiol is greater than four.

6. A process as described in claim 5 wherein the photocurable composition in said photocurable layer is comprised of 2 to 98 parts by weight of said polyene, 98 to 2 parts by weight of said polythiol, and 0.0005 to 50 parts by weight photocuring rate accelerator based on 100 parts by weight of said polyene and said polythiol.

7. A process as described in claim 6 wherein said polyene composition has a molecular weight in the range of 50 to 20,000; has a viscosity ranging from essentially 0 to 20,000,000 centipoises at 130°C.; and has a general formula: $[A]-(X)_m$ wherein X is a member of the group consisting of



and $R-C \equiv C-$; m is an integer of at least two; R is independently selected from the group consisting of hydrogen, halogen, and an organic compound selected from the group consisting of aryl, substituted aryl, aralkyl, substituted aralkyl, cycloalkyl, substituted cycloalkyl, alkyl and substituted alkyl groups containing one to four carbon atoms; and A is a polyvalent polymeric organic moiety free of (1) reactive carbon-to-carbon unsaturation, and (2) unsaturated groupings in terminal conjugation with X.

8. A process as described in claim 7 wherein the polyene has a molecular weight in excess of 300.

9. A process as described in claim 7 wherein the two or more reactive ene groups are located terminally in the molecule, or where the two or more reactive ene groups are conjugated with other unsaturated groups.

10. A process as described in claim 7 wherein the said polythiol has a molecular weight between about 50 and about 20,000, and has a viscosity between slightly above zero and about 20,000,000 centipoises at 70°C.

11. A process as described in claim 7 wherein said polyene is prepared from allyl alcohol, polyalkylene ether glycol and tolylene diisocyanate.

12. A process as described in claim 6 wherein the photocurable composition contains 0.0005 to 5.0 parts by weight of an antioxidant, 0.05 to 25 parts by weight of a pigment, 1.0 to 50 parts by weight of a plasticizer, and 0.5 to 100 parts by weight of a filler, each of said ingredients being based upon 100 parts by weight of said polyene and said polythiol.

13. A process as described in claim 9 wherein said antioxidant is 2,6-di-tert-butyl-4-methylphenol.

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14. A process as described in claim 1 wherein said photocured coating is ground and buffed.

15. A process as described in claim 1 wherein said radiation is electron beam radiation from a source which is located essentially perpendicular of said rotating core and wherein photocurable composition is

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coated onto said rotating core from a source which is located at a point opposite the radiation source.

16. An article of manufacture consisting of a cylindrical core coated with a cured polythioether.

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