Oct. 27, 1964 C. S. HERRICK 3,154,432

COATED POLYCARBONATE RESIN RECORDING SHEET

Filed June 15, 1961

Fig. 1.

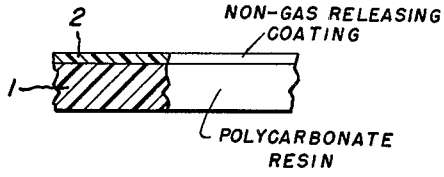


Fig. 2.

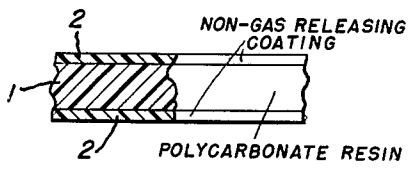


Fig. 3.

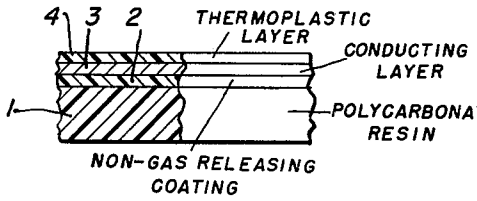


Fig. 4.

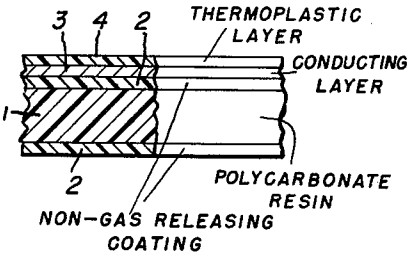
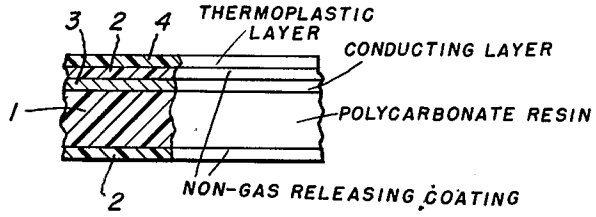


Fig. 5.



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His Attorney.

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3,154,432

COATED POLYCARBONATE RESIN RECORDING SHEET

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9 Claims. (Cl. 117—211)

This invention is concerned with coated polycarbonate resins and recording media for the storage of information in a form of physical deformations. More particularly, the invention relates to both a coated polycarbonate resin and a recording medium using such a coated polycarbonate resin comprising (1) a thermoplastic polymer layer, (2) a supporting base polycarbonate resin layer, and (3) an intermediate barrier thermoset polymer layer between the thermoplastic layer and the supporting base layer. These recording media may have a conducting layer intermediate the base layer and the thermoplastic polymer layer. These recording media can be employed in the form of tapes, sheets, slides, disks, etc., suitable for recording, storing and reproducing photographic images and technical data wherein the thermoplastic layer is the medium in which the image and data are recorded, stored and reproduced.

In the copending applications of William E. Glenn, Jr., Serial No. 698,167, filed November 22, 1957, and Serial No. 783,584, filed December 29, 1958, both now abandoned, both of which are assigned to the same assignee as the present invention, are disclosed and claimed an electronic method and apparatus for recording, storing and reproducing photographic images and technical data. According to this method, technical data and photographic images are first converted electronically into coded signals. These signals are further reduced to variations in the intensity of a beam of electrons, and the electron beam with its negatively charged particles is used to scan a special surface so as to introduce onto this surface a pattern of negative charges (from the electrons deposited) which arrange themselves in accordance with the data or image to be recorded. This pattern of electric charges is essentially the "negative" of the composite film, sheet, slide, etc., which is later developed by converting the pattern of electric charges on the heat-deformable layer to a pattern of depressions, ridges, etc., that can be observed optically.

This conversion can be achieved by heating the composite article or recording medium, particularly the surface thereof with, for instance, direct application of heat or by heat generated by radio frequency energy acting on a conducting layer, whereby the heat causes only the top thermoplastic negatively charged layer to fuse or melt, and become liquid. When this happens, the negative charges are attracted to the conducting layer positioned under but not necessarily in contact with the thermoplastic layer, thus deforming the surface of the thermoplastic upper layer into various depressions, hills, ridges, etc. Thereafter, the heated surface is cooled or allowed to cool immediately to set or solidify these hills, ridges, and other deformations in the thermoplastic layer. The recording medium thus treated can now be read or projected visually by passing a beam of light through it in cooperation with a special optical system for conversion into an image or can be optically converted into the desired information or data in the form of electrical signals. The image can be viewed directly, projected on a screen, transmitted electronically for viewing on a television screen elsewhere, or can be simply stored on film. An additional description of the method for recording in the manner described above can be found in an article by William E. Glenn, Jr., in "Journal of Applied Physics," December 1959, pages 1870–1873.

Because the thermoplastic layer is capable of being heated to the liquid state (at which time it develops the surface deformations by action of the induced electric field on a charged portion of the liquid and the pattern of ripples thus produced frozen into a permanent record by promptly cooling the liquid thermoplastic layer to the solid state), it is possible to employ such recording material many times over by merely subjecting the surface layer to the action of heat at a temperature high enough to cause fusion of the upper layer to a smooth surface, thus "erasing" the information stored in the aforesaid thermoplastic layer. In addition to the ability to reuse repeatedly the recording medium, the latter can also be employed as a "master copy" for duplication by techniques similar to phonograph disk stampings.

In one form of the invention described in the above Glenn applications, the retrieval of information is accomplished by projecting a beam of light through the entire recording medium, thus necessitating that the medium be optically transparent. Additionally, other methods of retrieval may be practiced wherein the information stored as light modifying deformations can be reproduced as a visible image from an opaque recording medium. Thus, an incident light beam can be projected onto deformations to produce a spatial light image by known optical reflection techniques.

In making the above types of recording media, care must be exercised as to the choice of backing which is used for making such recording media. Ordinarily, this backing or support for the recording thermoplastic layer is prepared from solid material which is thermally stable at the liquid temperature of the recording layer, and includes both flexible and rigid materials. Various materials may be used as the support layer for the recording medium including polyethylene terephthalate film, cellulose acetate, glass, opaque layers prepared from such materials as metals, or filled phenol-aldehyde resins, unsaturated polyester resins, ceramics, etc.

One form of supporting layer which has been found especially useful in making recording media of the type described above are those made from polycarbonate resins. These resins have exceptionally good flexibility, strength, good adhesion to the conducting layer (if it is present), and clarity as well as good resistance to elevated temperatures at which the thermoplastic layer containing the recorded information is heated to effect deformation of the charge patterns introduced into the thermoplastic layer. Furthermore, these polycarbonate resins are substantially free of volatiles which are harmful to the remainder of the elements of the recording medium.

However, several difficulties have been encountered in using these polycarbonate resins as supporting layers. In the first place, these polycarbonate resins have a susceptibility to being deleteriously affected by solvents, particularly aromatic solvents, which are used as solvents for the thermoplastic polymer layer when solutions of the thermoplastic polymer are employed to coat the supporting base layer and any other intermediate layer such as a metal conducting layer (for instance, metals, metal oxides, metal salts, etc.). Thus, it has been found that these polycarbonate resins tend to crack, swell, deform, and lose dimensional stability in the presence of solvents used to dissolve the thermoplastic composition when processing these recording media for applying a thermoplastic layer to the balance of the recording medium. The swellings and cracks which are produced in the polycarbonate resin layer are large compared with the size of the deformations caused in the thermoplastic layer by the signal modulated electron beam. When such a recording medium is used in a read-out system involving light transmitted through the recording medium, the light scattered by the swellings and cracks is visible as part

of the projected image and interferes with faithful reproduction of the matter which has been recorded on the thermoplastic layer by the electron beam.

In addition it has also been found that in the preparation of the polycarbonate base layer, either in laying down films or other supporting forms of the polycarbonate resins, or even while handling the polycarbonate resin, slight cracks, elevations, depressions, often appear even in spite of the most careful handling. If such defects in the supporting layer are not removed or minimized to the greatest extent possible, it will be found that there will be a faulty reproduction of the formation stored in the thermoplastic layer. Thus, heretofore, it has been necessary to pay particular attention and use special techniques to prepare the surface of the usual support layers and this applies particularly to polycarbonate resin layers which contact the recording or thermoplastic layer, to insure a smooth, flat, recording surface in the supporting layer, since defects in the supporting surface tend to be reproduced in the top surface of the thin recording layer. Often it is necessary to employ specialized techniques such as grinding, solvent polishing, etc., in order to remove these defects and to close up any cracks which may appear in the polycarbonate resin layer. It is therefore apparent that it would be desirable to provide by a more simplified means a smooth flat exterior surface on the polycarbonate resin supporting layer which can then contribute to the faithful reproduction of the information deposited in the thermoplastic layer.

One of the inherent advantages in employing polycarbonate resins as the supporting base member for the above described recording media is the fact that there are generally little or no volatiles in the polycarbonate resin layer which will adversely affect the entire recording medium and particularly the thermoplastic polymer layer, either during the actual introduction of the information and storage of the thermoplastic layer, or during the retrieval of such information by any means, many of which are described in the above Glenn applications. Furthermore, no plasticizers are required for these polycarbonate resins so that migration of the plasticizer to the recording layer will in no way affect the thermoplastic recording layer.

Finally, it is further desirable to be able to use polycarbonate resins as a supporting member because in many instances intermediate metals, metal oxides, or metal salts, of a conducting nature, are interposed between the supporting base member and the thermoplastic recording layer to serve as a conducting layer (which should be thin enough to be optically clear if interposed between the base supporting layer and the thermoplastic layer) which can be subjected to radio frequency energy as a means for heating the thermoplastic layer. This conducting layer becomes positively charged beneath the thermoplastic layer and when the thermoplastic layer is heated it causes the thermoplastic material to become fluid and deformable; at the same time, the deposits of negative charges on the top of the thermoplastic layer are attracted to the positively charged conducting layer thus deforming the thermoplastic surface of the film. Among such conducting layers may be mentioned the various metals, for instance, iron, chromium, tin, nickel, etc.; metallic oxides such as stannic oxide, cuprous oxide, etc.; salts, for instance, cuprous iodide, cuprous sulfide, etc.

When such a conducting layer is applied to the polycarbonate resin substrate, the susceptibility of the polycarbonate resin to attack by the solvents used for the thermoplastic layer causes the above-described swellings and crackings. These swellings and crackings can also be caused by penetration of the conducting layer by the solvent used for the thermoplastic polymer, and such swellings and crackings are often severe enough to burst the conducting layer resulting in numerous small areas

of the recording medium which are not covered by electrically conducting material. These discontinuities (ruptures) in the conducting layer interfere with the proper functioning of the electron beam as it records the signal across affected areas. This interference occurs whether the read-out method uses either transmitted or reflected light.

It is therefore the principal object of this invention to provide an improved recording medium for the storage of information in the form of light modifying deformations employing polycarbonate resins as the supporting base layer.

It is another object of the invention to provide a stable, reusable deforming medium for the storage of information in the form of light modifying deformation employing a polycarbonate base layer which does not adversely affect the thermoplastic recording layer and which also has good heat resistance and flexibility.

It is a still further object of the present invention to provide a protection barrier for polycarbonate resins which are susceptible to attack by certain solvents.

A further object of the invention is to provide a polycarbonate resin film having improved optical quality.

Other objects of the invention will become apparent from the description which follows and when considered in the light of the accompanying drawing.

Briefly, the above objects of my invention are achieved by interposing a barrier layer of non-gas releasing thermoset polymer on the polycarbonate resin and in the case of the recording media between the recording thermoplastic layer and the supporting base polycarbonate resin layer. This barrier layer is intended to coat, enclose or encapsulate the polycarbonate resin layer so as to prevent it from being adversely attacked by any solvent used with the thermoplastic polymer when coating the base layer or the base layer in combination with a conducting layer, a description of which is found above.

In addition, I employ for the barrier layer a potentially thermosetting material which uses as its solvent a material which can exercise a slight solvation action on the surface of the supporting polycarbonate resin layer so as to cause a slight flow of the surface of the polycarbonate resin to close up any cracks or gaps which may be present on the surface thereof, and also to cause smoothing out of any harmful elevations or any other imperfections on the surface of the polycarbonate resin layer. This action improves substantially the optical quality of the polycarbonate resin film.

Advantageously, the potential thermosetting non-gas releasing polymer in suitable solvent is one which when applied to the polycarbonate resin layer can be cured to the thermoset, infusible, insoluble state at temperatures which do not affect the physical or chemical properties of the polycarbonate resin layer, tenaciously adheres to the polycarbonate resin layer, and does not adversely affect the optical characteristics of the recording medium which will be derived from the coated polycarbonate resin layer. Additionally, the thermoset coating applied to the polycarbonate resin should have good adhesion to the thermoplastic layer and also should have good adhesion to the conducting layer since one of the specific embodiments of this invention includes treating an assembly composed of the polycarbonate resin layer containing a thin coating of a conducting layer, and coating this composite assembly with the potentially thermosetting polymer and thereafter effecting cure of the latter at the temperatures required to accomplish this result. Primarily, it is further important that the thermoset coating should not adhere to any surface with which it may come in contact in the recording medium such as, for instance, when making tapes, since in the rolled up state the thermoset polymer will come in contact with the thermoplastic layer and it is important that there be no adhesion and that the release characteritsics should be complete between the thermoset polymer and the thermo-

plastic layer, as well as having good release characteristics in the event that the thermoset layer should come in contact with itself.

For a more ready understanding of the invention, reference is made to the appended drawings illustrating several practical embodiments thereof. In these drawings, FIGS. 1 and 2 are cross-sectional views of polycarbonate resin containing coatings of thermoset, non-gas-releasing polymers, while FIGS. 3, 4 and 5 are concerned with the recording media employing the barrier, thermoset, non-gas-releasing polymer for the purposes outlined above.

Referring particularly to FIG. 1, the polycarbonate resin base 1 is shown with a thermoset, non-gas-releasing polymer coating 2 thereon to act as a barrier for any attack of the polycarbonate surface, and for reducing imperfections in the surface of the base which would cause optical interference.

FIG. 2 shows a polycarbonate resin base 1 which is coated on both sides with a film of the thermoset, non-gas-releasing polymer 2.

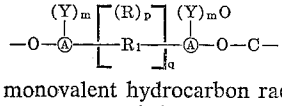
FIG. 3 shows a recording medium composed of a polycarbonate resin base or substrate 1, a protective barrier layer of the thermoset, non-gas-releasing polymer 2, a conducting layer which may be either metal, metal oxide, or other metal compounds 3, and a thermoplastic layer 4 upon which the recording by means of electron bombardment is carried out.

FIG. 4 is another embodiment of a recording medium in which the polycarbonate resin base 1 is surrounded on two sides by the protective barrier coating of the non-gas-releasing, thermoset polymer 2, there being superposed on the non-gas-releasing polymer a conducting coating 3 and upon the conducting coating is placed the thermoplastic layer 4 on which the recording will be made.

Finally, FIG. 5 is concerned with a still further embodiment of the claimed invention directed to a recording medium in which the base layer of polycarbonate resin 1 is coated on the underside by the thermosetting, non-gas-releasing polymer 2 and contains a conducting layer 3 directly superposed on the polycarbonate resin. Thereafter, another film of the thermoset barrier polymer 2 is placed on the conducting layer and on top of the latter barrier layer is placed the recording thermoplastic layer 4.

The solid polycarbonate backing materials which are employed in the practice of the present invention because of their heat resistance, strength, inertness, flexibility, and resistance to radiation comprises a linear polymer comprising the recurring structure unit of the formula

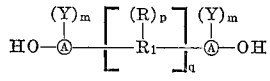
(I)



where R is a monovalent hydrocarbon radical; R_1 is selected from the group consisting of an alkylene and an alkylidene residue; A is the residue of an aromatic nucleus; Y is a chemical constituent selected from the group consisting of (*a*) inorganic atoms, (*b*) inorganic radicals, and (*c*) organic radicals; *m* is a whole number equal to from 0 to a maximum determined by the number of replaceable nuclear hydrogens substituted on the aromatic hydrocarbon residue A; *p* is a whole number equal to from 0 to a maximum determined by the number of replaceable hydrogens on R_1; and *q* is a whole number equal to from 0 to 1 inclusive.

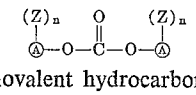
One method of preparing these resins comprises effecting reaction between (1) a dihydroxydiaryl compound of the formula

(II)



and (2) a diaryl carbonate of the formula

(III)



where R is a monovalent hydrocarbon radical; R_1 is selected from the group consisting of an alkylene and an alkylidene residue; A is the residue of an aromatic nucleus; Y and Z are chemical substituents selected from the group consisting of (*a*) inorganic atoms, (*b*) inorganic radicals, and (*c*) organic radicals, (*a*), (*b*) and (*c*) being inert to and unaffected by the reactants and by the reaction of the dihydroxydiaryl compound and the diaryl carbonate; *m* and *n* are whole numbers equal to from 0 to a maximum equivalent to the number of replaceable nuclear hydrogens substituted on the aromatic hydrocarbon residue A; *p* is a whole number equal to from 0 to a maximum determined by the number of replaceable hydrogens on the alkylene or alkylidene residue; and *q* is a whole number equal to from 0 to 1 inclusive.

In the above formula for the dihydroxydiaryl compound (hereinafter employed as a designation for the compound defined in Formula II), the inert substituents designated by Y on each aromatic hydrocarbon residue may be the same or different, and R's may also be the same or different; the number of Y's on each respective aromatic hydrocarbon nucleus residue A may also be varied if desired so that a symmetrical or an unsymmetrical compound be formed. The Z's in the diaryl carbonate defined by Formula III may also be the same or different, and the number of substituents represented by Z may be the same on each aromatic nucleus A, or may vary depending upon the degree of substitution desired on each aromatic residue A.

Among the monovalent hydrocarbon radicals which R may represent are, for instance alkyl radicals (e.g., methyl, ethyl, propyl, isopropyl, butyl, decyl, etc.), aryl radicals (e.g., phenyl, naphthyl, biphenyl, tolyl, xylyl, ethylphenyl, etc.), aralkyl radicals (e.g., benzyl, phenylethyl, etc.), cycloaliphatic radicals (e.g., cyclopentyl, cyclohexyl, etc.), as well as monovalent hydrocarbon radicals containing inert substituents thereon, for instance, halogens (e.g., chlorine, bromine, fluorine, etc.). Among the aromatic nuclei which A may represent are, for instance the aromatic hydrocarbon residues based on benzene, biphenyl, naphthalene, anthracene, etc. The final configuration of this aromatic hydrocarbon residue in the molecule is determined by the nuclearly-substituted hydroxyl groups, together with any nuclearly-substituted hydrogen atoms and the number of inert substituents represented by either Y or Z.

Examples of R_1 as an alkylene or alkylidene residue are, for instance, methylene, ethylene, propylene, propylidene, isopropylidene, butylene, butylidene, isobutylidene amylene, isoamylene, amylidene, isoamylidene, etc. When *p* is zero, the valence requirements of the carbon skeleton of the alkylene or alkylidene residue are completely satisfied with hydrogens. When *p* is greater than zero, hydrogens fulfill the valence requirements of the carbon skeleton not satisfied by the R's.

Among the inert substituents which Y and Z may represent are, for instance, halogens (e.g., chlorine, bromine, fluorine, etc.); organoxy radicals of the formula OW, where W is a monovalent hydrocarbon radical similar to those recited for R; and monovalent hydrocarbon radicals of the type represented by R. Other inert substituents included within the scope of Y and Z, such as the nitro group, may be substituted on the aromatic nuclear residue A without departing from the scope of the invention.

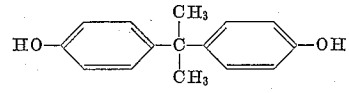
In the above formulae, *m* and *n* may be zero whereby the aromatic nuclear residues A will be unsubstituted except for the hydroxyl group in regard to Formula II, or else there may be a plurality of substitutions of inert substituents on the aromatic nuclear residues depending upon the number of nuclearly-bonded hydrogens remaining on A, taking into consideration the presence of the hydroxyl group in Formula II. Where *q* is zero the aromatic nuclei will be directly joined without the presence of an alkylene or an alkylidene bridge.

The position of the hydroxyl groups, Y, and Z on the

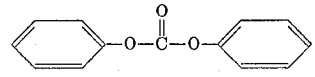
aromatic nuclear residue A, may be varied in the ortho, meta or para positions, and the groupings may be in a vicinal, asymmetrical, or symmetrical relationship, where two or more of the nuclearly-bonded hydrogens of the aromatic hydrocarbon residue are substituted with, for instance, Y, the hydroxyl group in Formula II.

Further examples of polycarbonate resins or poly (dimonohydroxy arylene alkane carbonates) may be found in the copending application, Serial No. 598,768 of Daniel W. Fox and Frank M. Precopio, filed July 19, 1956, and assigned to the same assignee as the present invention. By reference this application is incorporated in the instant application. Other polycarbonate resins and methods of manufacture may be found in U.S. Patents 2,964,794 and 2,950,266. A preferred polycarbonate resin which is used in making the recording medium employing the polycarbonate resin as a base member is commercially available and produced by the General Electric Company under the registered trademark "Lexan."

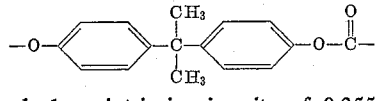
One method of preparation of such polycarbonate resins comprises reacting equimolar ratios of Bisphenol-A having the formula



with diphenyl carbonate



Specifically, 114 parts, by weight, Bisphenol-A and 107 parts diphenyl carbonate were charged to an oil bath heated reactor equipped with a stirrer, an inert gas inlet, and a condenser-receiver system connected to a vacuum. Nitrogen was allowed to enter the reactor system, and heat was applied so that initial distillation of phenol began when the bath temperature reached about 185–190° C. (which was about one-half hour after heating) and continued rapidly for 1 to 1½ hours at this temperature and a pressure of about 10 mm. during which time most of the phenol was evolved. The temperature of the heating bath was then slowly raised to 290° C. and held at this temperature for about 5 hours during which time the viscosity of the reaction mixture increased. The polycarbonate resin thus obtained was found to have a melting point of about 280–300° C. and comprised recurring units of the formula



This resin had an intrinsic viscosity of 0.355 as determined in p-dioxane at a temperature of about 30.3° C. using an Ostwald viscometer. A thin tape was prepared from the polycarbonate resin by forming a solution thereof and depositing the solution on a flat surface and thereafter allowing the solvent to evaporate. The film thus obtained was cut to tape size about 4 mils thick and used in the examples below.

Suitable polymers for the thermoset layer used to coat the polycarbonate tape are film-forming organic materials having a repeating unit molecular structure of at least two units which can be cross-linked to a non-gas-releasing solid that is infusible and insoluble at the elevated temperatures (about 85 to 150° C.) employed to record the information on the recording layer. The thermoset polymer must also be capable of being cured in situ when deposited to provide a continuous layer which adheres to the polycarbonate substrate sufficiently to prevent delamination during use of the recording medium. Preferred thermoset polymers for the thin recording tapes described in the above embodiments are organic polymers which are sufficiently soluble so that films of about 0.5 to 1 micron thickness can readily be deposited from a solution of the polymer. Although thermoset films up to 4 microns thickness have been found satisfactory to provide all the advantages hereinbefore described, it may be desirable for a particular purpose to employ thermoset layers of greater thickness. For greater thickness thermoset layers (and often in thinner thicknesses) it is desirable to select optically transparent polymers so that retrieval of the information recorded in the thermoplastic layer can be accomplished by transmission of a light beam through the entire recording medium as well as by optical reflective methods and lithographic printing.

Typical thermoset polymers having the desirable properties can be selected from the general class of formaldehyde condensation product, including phenol-formaldehydes, urea-formaldehyde resins, and melamine-formaldehyde resins, etc. Included among the barrier non-gas-releasing polymers which may be employed in the practice of the present invention, may be mentioned the organopolysiloxanes containing an average of from about 1.1 to 2.0 organic groups per silicon atom, as for instance those mentioned in Rochow Patents 2,258,218–2,258,222, issued 1941, which can be prepared by the hydrolysis of silanes of the type R_nSiX_{4-n} where R is a monovalent hydrocarbon radical (e.g., methyl, ethyl, phenyl, chlorophenyl, etc.), and n is an integer of from 1 to 3, the organosilanes so being chosen that they will contain an average of from about 1.1 to 2 silicon-bonded, monovalent organic radicals per silicon atom. In the higher range of organic to silicon ratios, these organopolysiloxanes are generally rubbery materials as, for instance, those described in U.S. Patent 2,448,756 of Maynard C. Agens, assigned to the same assignee as the present invention. Additionally, methyl phenyl polysiloxane elastomers of the type described in Sprung Patent 2,484,595, also assigned to the same assignee as the present invention, may also be used in suitable solvents with peroxide curing agents for the coating of the polycarbonate resin.

Alkyd resins may also be used as the coating material. These can be prepared by interaction of an acidic compound selected from the group consisting of polycarboxylic acids and anhydrides having from 2 to 3 carboxyl radicals per molecule and polyhydric alcohols having from 2 to 4 hydroxyl radicals per molecule. The preferred compositions are alkyd resins obtained from the interaction of, for instance, phthalic anhydride, glycerine, and/or pentaerythritol. These alkyds are preferably further modified by the presence of a drying oil such as linseed oil acid, soya bean oil acid, dehydrated castor oil acid, tung oil acid, the oiticica oil acids, poppy seed oil acid, sunflower seed oil acid, etc. Any of the drying oils whose acid derivatives are listed above can be employed in this invention. The percent drying oil content of the above-mentioned resins may vary from 10 to 80 percent with 25 to 75 percent being preferred. Resins prepared by the interaction of polyhydric alcohols having from 3 to 4 hydroxyl radicals per molecule or any of the above-mentioned drying oil acids may also be utilized.

In addition to the above, phenol-formaldehyde resins or modifications thereof, which are soluble in organic solvents and advantageously soluble in drying oils such as those normally employed in the paint and varnish industry, may be utilized in the present invention. The term "phenol" as employed herein includes both phenol and substituted phenols. Other aliphatic or aryl substituents may be present on the phenol, provided the resulting resin is soluble in a suitable solvent. The phenol-aldehyde resin (where the aldehyde may be, for instance, formaldehyde, furfural, acetaldehyde, etc) should be heat reactive in order that one may obtain thermoset polymeric coatings. Examples of resins which are operative here are phenol-formaldehyde resins, p-tertiarybutyl phenol-formaldehyde resins, p-tertiaryamyl phenol-formaldehyde resins, and p-phenylphenol-formaldehyde resins, etc.

Phenol-formaldehyde resins may be further modified with from 10 to 40% of a drying oil acid, many examples of which have been mentioned above.

The solvents used are those which ordinarily are solvents for the thermosetting polymer and also are advantageously, though not necessarily, capable of exercising some solvating action on the polycarbonate resin layer. One of the embodiments of the invention involves the use of special solvents with the thermosetting polymer to effect smoothing out of the polycarbonate resin layer in the event that it requires it, without adversely affecting the polycarbonate substrate. However, it should be understood that one of the prime problems to which the present invention is addressed is to obtain a thermosetting coating on the polycarbonate resin layer, and where the polycarbonate resin layer is smooth and without any surface defects, the necessity for a solvating solvent with the thermosetting polymer would of course be unnecessary.

Among the solvents which may be employed with the potentially thermosetting resins may be mentioned, for instance, the Carbitols (e.g., ethyl Carbitol, butyl Carbitol, etc.), the Cellosolves (for example, methylcellosolve, ethyl Cellosolve, butyl Cellosolve, dibutyl Cellosolve, etc.), diacetone alcohol, methyl acetate, amyl acetate, ethyl alcohol, cresol, benzene, toluene, secondary butyl acetate, isopropyl acetate, Cellosolve acetate, petroleum spirits, petroleum naphtha, acetone, and isopropyl alcohol. The concentration of the thermosetting polymer in the solvent may be varied widely depending on the thickness of the coating desired on the polycarbonate resin surface, and also depending on the resin used and its degree of solubility in the solvent. Generally, solvent concentrations of from about 5% to 30%, by weight, of the thermosetting resin, based on the total weight of the solvent are advantageously employed.

Various thermoplastic compositions may be employed as the thermoplastic layer for the recording medium. Generally, the thermoplastic layer must be optically clear and must be stable under moderate electron bombardment from the electron high voltage accelerating apparatus used to form the charge pattern on the surface of the thermoplastic layer. In addition, the thermoplastic layer preferably is flexible and has a maximum vapor pressure of 10^{-5} to 10^{-6} mm. mercury when in the liquid state; it must also be stable at the elevated temperatures at which it will be deformed by the heat necessary to "develop" the charge on the thermoplastic layer. Moreover, the thermoplastic layer must be capable of having a fairly sharp melting point in order that the developing of the proper image on the thermoplastic layer proceeds with a minimum of control difficulties. Generally, the thermoplastic layer should be solid at temperatures of at least 65° C. but should be capable of being converted to the liquid or fused state at temperatures of at least 85° C. If the supporting or base layer is resistant to temperatures well above 150° C. or higher, as the polycarbonate base layer is capable of withstanding, it is then possible to use thermoplastic compositions having softening or liquid points well above the minimum 85° C. recited above. This is the reason why the use of polycarbonate resins as the supporting or base layer appears so attractive in making these recording media. In addition, the recording medium should have good adhesion to the back material or have good adhesion to the intermediate conducting layer (when it is so employed). Where the recording medium is in the form of a tape, and thus will be rolled upon itself and stored, it is important that the thermoplastic layer be substantially free of cold flow and that the thermoplastic layer be non-tacky and should not stick to any surface with which it might come in contact in the rolled-up state.

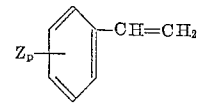
Among the thermoplastic layers which may be employed in the practice of the present invention are, for instance, polystyrene, of the desired softening point (which means that it have the proper molecular weight), mixtures of polystyrene, m-terephenyl and a copolymer of 95 weight percent butadiene and 5 weight percent styrene, etc., as is more particularly recited in the copending application of William E. Glenn, Jr., Serial No. 8,842, filed February 15, 1960, and assigned to the same assignee as the present invention, now U.S. Patent 3,113,179.

A particularly desirable thermoplastic layer is made from a mixture of ingredients comprising (1) an organopolysiloxane and (2) a thermoplastic solid (that is, solid at room temperature), aryl polymer selected from the class consisting of (*a*) polyarylene ethers, (*b*) a polystyrene, and (*c*) mixtures of (*a*) and (*b*). One component of this mixture of ingredients used to make the thermoplastic composition is an organopolysiloxane having the formula

$$R_mSiO_{\frac{4-m}{2}}$$

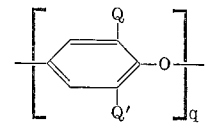
where *m* is a value from 1 to 2.1 and R is a monovalent organic radical (which may be the same or different), at least 40% of the silicon bonded R groups being aryl groups. Among the values which R may be are, for instance, cyclopentyl, cyclohexyl, methyl, ethyl, propyl, phenyl, tolyl, ethylphenyl, benzyl, phenylethyl, etc.

Another component of the mixture of ingredients used to make the aforesaid thermoplastic composition is a polystyrene material having the formula



where Z is a member selected from the class consisting of hydrogen, halogen, and alkoxy, and *p* is a whole number equal to from 0 to 3.

The aryl polymer can also be a thermoplastic composition composed of recurring units of the formula $\dagger W—O\dagger_q$ where W stands for an arylene radical, for instance a divalent phenyl radical, either substituted or unsubstituted, and *q* is a whole number equal to at least 10 or more, e.g., up to 10,000 or more. Thus, W can be phenylene, chlorophenylene, naphthylene, etc. A group of aryl polymers which can be advantageously employed comprises those having the formula



wherein the oxygen atom of one unit is connected to the benzene nucleus of the adjoining unit, *q* is a positive integer equal, for instance, to at least 10, e.g., from 100 to 5,000 or more, Q is a monovalent substituent selected from the class consisting of hydrogen, aliphatic hydrocarbon radicals free of tertiary α-carbon atoms, halogen, aralkyl, alkaryl, and aryl radicals, Q′ is a monovalent substituent which may be the same as Q and in addition may be a hydrocarbonoxy radical, an aliphatic tertiary α-carbon atom, etc.

Examples of the mixtures of the organopolysiloxane and the aryl polymer are more particularly disclosed and claimed in the copending application of Edith M. Boldebuck, Serial No. 8,587, filed February 15, 1960, and assigned to the same assignee as the present invention, now U.S. Patent 3,063,872 issued November 13, 1962. This application, which by reference is made part of the disclosures of the instant application, contains additional compositions and proportions of ingredients, as well as methods for preparing these compositions designed to form the mixture of ingredients advantageously employed in the thermoplastic layer of the recording media herein described. In choosing the thermoplastic layer which I

apply to the recording medium, care should be exercised that it satisfies the various conditions for the thermoplastic layer recited above.

When employing an intermediate conducting layer for recording tapes of the preferred embodiment of the present invention, in order to provide means for heating the recording layer by radio frequency or induction heating, a very thin film of the metal or metallic compound having a resistivity advantageously between about 1,000–10,000 ohms per square centimeter, is advantageously employed. The preferred conducting films are approximately 0.001 to 0.01 micron thick and advantageously are no thicker than is required to obtain the transparent film thereon. Among such conducting layers which may be mentioned are various metals, for instance, iron, chromium, tin, nickel, etc.; metallic oxides, such as stannic oxide cuprous oxide, indium oxide, etc.; salts, for instance, cuprous iodide etc.

The thickness of the thermoplastic layer can vary widely, but advantageously is approximately 4 to 20 microns thick. The base layer thickness can also vary widely as long as it has the proper electrical and radiation resistance, flexibility, strength, heat resistance, etc. Generally, the thickness of the supporting layer of polycarbonate resin can be from a few microns in thickness to as much as 50 to 400 microns or more in thickness.

The conducting layer is advantageously applied to the polycarbonate backing coated with the barrier layer or directly to the barrier layer by the well-known method of volatilizing the metal or metal compound in a vacuum at elevated temperatures and passing the backing through the vapors of the metal or metal compound so as to deposit an even, thin, optically clear, adherent film of the metal or metal compound on the backing and preferably while the entire assembly is still under vacuum. One method for applying a metal salt conducting layer to the backing is found in U.S. Patent 2,756,165, Lyon. Thereafter, a solution of the thermoplastic composition is applied to the surface of the conducting layer, and the solvent evaporated to deposit a thin film of the thermoplastic composition on the conducting layer.

The particular solvents employed for the thermoplastic composition may be varied widely and will depend on the type of polymers and resinous compositions employed in the mixture of ingredients. Included among such solvents are aromatic hydrocarbon solvents, e.g., toluene, xylene, benzene, etc. Solids weight concentrations of from 10 to 30 percent of the thermoplastic composition in the solvent are advantageously used.

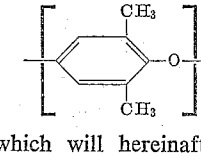
A preferred recording medium of the invention is a tape, which comprises a recording layer, a thermoset inner layer, a conducting inner layer, and a supporting base layer of polycarbonate resin. The polycarbonate base layer can be coated on both sides (and even its edges) by a thermoset non-gas-releasing polymer such as a suitable phenolformaldehyde resin. The barrier layer surrounding the polycarbonate base layer can encase not only the base layer itself but also the adhered metallic conducting layer so that when the thermoplastic layer is applied to the base layer and conducting layer combination, the solvent used for the thermoplastic composition will not attack the polycarbonate resin layer while at the same time maintaining the integrity of the metallic conducting layer.

The thickness of the thermoset layer which is applied to the polycarbonate base member or to the combination of the polycarbonate base member and the metallic conducting layer should be maintained between about 0.5 to about 4 microns in thickness. Thinner thermoset layers lack continuity and they will not provide an adequate barrier to prevent attack of the polycarbonate resin layer. Thermoset layers greater than about 4 to 10 microns in thickness may cause loss in flexibility and serve no useful purpose especially since it is found that they absorb so much heat that the recording layer is liquefied during the recording process only with extreme difficulty. If the thermoset layer is of proper thickness within the ranges preferably recited above, this helps to diffuse the heat during the recording which minimizes localized overheating in the recording layer due to localized differences in the resistivity of the conducting layer. The thickness of the thermoset layer can easily be controlled in the desired range by depositing a film from 10 to 30% solids concentration of an organic liquid solution of the thermosetting polymer.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

The organopolysiloxane polymer forming one of the ingredients of the thermoplastic layer employed in the following examples was a diphenyl silicone polymer (hereinafter so designated) obtained by melting 600 parts octaphenylcyclotetrasiloxane in a flask under nitrogen sparge and when the liquid polysiloxane was at a temperature of about 230° C., 1 part cesium hydroxide was added and while stirring, the temperature was slowly increased to 260° C. for 1 hour. A second portion of 0.5 part cesium hydroxide was added and heating was continued at 260–270° C. for 1½ hours longer. At this time, a small amount of iodine was added to the hot reaction mixture until the purple color was no longer present evidencing that the cesium hydroxide was completely neutralized. The excess iodine was allowed to sublime, and the reaction mixture was then cooled to about 125° C. and 433 parts toluene was added and stirred into the viscous melt. The solution was allowed to stand for 72 hours and the crystalline material that formed was filtered off. Residual solvent was then removed from the polymer by distillation at atmospheric pressure followed by distillation in vacuum at about 125° C., with a slow stream of nitrogen passing through the viscous melt to remove the final trace of solvent. This yields a hard transparent diphenyl polysiloxane polymer having a molecular weight of approximately 1275 by ebullioscopic measurement in benzene. The polymer melted to a liquid at around 80° C.

The arylene ether polymer (which had an intrinsic viscosity of about 0.6 deciliter per gram and a molecular weight of about 20,000–25,000), forming the other ingredient of the thermoplastic layer, was prepared by passing oxygen for 75 minutes into a reaction mixture containing 20 parts 2,6-dimethylphenol, 0.14 part cuprous chloride (Cu_2Cl_2), about 19.8 parts benzene and 23 parts pyridine. During the course of the reaction the temperature was held to a maximum of 40° C. After the reaction, the mixture was diluted with 616 parts benzene and the product was precipitated by pouring the reaction mixture into about 2014 parts methanol containing about 8 parts HCl, and the polymer was then separated by filtration. The product poly-(2,6-dimethyl-1,4-phenylene) ether was characterized by the recurring structural unit of the formula



This product (which will hereinafter be identified as "phenylene ether polymer") had a melting point in excess of 250° C. It was soluble in such solvents as benzene, toluene, xylene, and chloroform.

The conducting layer about 0.001 to 0.1 micron thick was applied to the coated or uncoated polycarbonate backing by the well-known method of volatilizing the metal or metal compound in a vacuum at elevated temperatures and passing the polycarbonate backing, whether coated or uncoated in proximity to the vapors of the metal or metal compound so as to deposit an even, thin, optically

clear, adherent film of the metal or metal compound on the coated polycarbonate backing containing the non-gas-releasing polymer while the entire assembly is still under vacuum. This conducting layer advantageously has a resistivity between about 100 to 10,000 ohms per square centimeter. Thereafter, a solution of the thermoplastic composition composed on a weight basis of 90 parts of the phenylpolysiloxane and 10 parts of the phenylene ether polymer was applied to the surface of the conducting layer where the conducting layer was directly adhered to the intervening barrier layer on the polycarbonate resin, or the solution of the thermoplastic composition was applied to the surface of the barrier layer which encased both the polycarbonate resin layer and the conducting layer. The solvent was then evaporated to deposit a thin film of the thermoplastic composition on the remainder of the tape member.

The actual writing on the thermoplastic surface (which was about 7–8 microns thick) was carried out as follows. An electron gun was mounted in a bell jar which fitted on an O-ring set into a horizontal base plate. The bell jar was set in place and the system was then evacuated. When the required high vacuum had been obtained, the metal plate carrying the sample was heated electrically to the desired temperature and the molten thermoplastic was then exposed to the electron beam. The electron beam was adjusted to sweep back and forth once in a linear path, irradiating an area 4 inches long and approximately 6 mils wide in a time interval of $\frac{1}{30}$ of a second. In the standardized test conditions, the beam was operated at a current of 0.1 microamp and with a 15 k.v. potential drop from filament to the sample holder (ground plate). In the single flash of $\frac{1}{30}$ second duration, 2×10^{10} electrons were delivered to a traced area of 0.024 square inch.

Example 1

A polycarbonate resin film about 4 mils thick was coated on both sides to a thickness of about 1 to 2 microns with a phenol-formaldehyde novolac resin (identified as Base Coat No. 107 resin manufactured by Schwartz Chemical Company, Inc., 326 West Seventieth Street, New York, New York) dissolved to a solids content of about 27% in butyl Cellosolve (or monobutyl ether of ethylene glycol). This phenol-formaldehyde resin which contained substituted alkyl groups could be readily cured at somewhat above room temperature to give a thermoset coating on the polycarbonate tape. A conducting transparent layer of chromium about 60 A. thick was evaporated on one surface of the phenolic polymer, in the manner described above. Thereafter, a 30 weight percent solution in a solvent mixture of benzene and toluene (where the benzene and toluene are in 1:2 volume ratio) of a mixture of the above described phenylpolysiloxane and a polyphenylene ether polymer was applied to the conducting surface on the polycarbonate tape to a thickness of about 7 to 8 microns. After coating the tape with the thermoplastic solution, the solvent was removed by first air-drying at about room temperature (about 22–24° C.) and then heating at about 100–140° C. to insure that all the solvent was removed. This tape was then examined and it was found that the polycarbonate substrate was entirely unaffected and showed no evidence of having been in any way harmfully attacked by the solvent used for the thermoplastic layer. Furthermore, imperfections (such as cracks and elevations) which were present in the polycarbonate polymer prior to coating with the phenolic polymer were removed by the action of the butyl Cellosolve. Additionally, it was noticed that this chromium conductor layer was firmly adhered to the phenolic resin layer. This tape was then placed in an electron beam in the manner described in the above-identified Boldebuck application and also more particularly recited and claimed in the aforementioned Glenn patent application, and was subjected to electron recording or writing in a vacuum. The charges on the thermoplastic layer were developed by passing the tape in such a manner that the polycarbonate layer was closest to the surface of a heated drum. The thermoplastic layer was allowed to cool to set or "freeze" the deformations on the surface of the thermoplastic layer. The information on the tape could be read out with the optical system described in the aforementioned Glenn application. The thermoplastic layer and films made therewith were optically clear, and had the proper electrical resistivity, toughness, and flexibility, as well as adherence to the phenolic resin encapsulating the polycarbonate resin base and the metallic conducting coating. The reduction in the number and severity of the imperfections by the above treatment of the polycarbonate resin film reduced markedly the interference with the recorded signal when it was read out by optical or electronic means.

Example 2

In this example, an electrically conducting layer of chromium about 60 A. thick was evaporated on a supporting member of polycarbonate resin film employing the same type film and methods for application of the chromium as were used in Example 1. The thermoplastic resin solution was applied similarly as was done in Example 1 to a thickness of about 8 microns, and the solvent allowed to evaporate. Examination of the tape thus prepared showed that the benzene-toluene solvent for the thermoplastic composition had penetrated the pores of the chromium layer causing extensive swelling and cracking in the polycarbonate film. Examination under the microscope showed that the chromium layer itself was ruptured in numerous places. When this tape was projected and viewed in a dark field optical system similarly as that employed in Example 1, only the general outline of a recorded signal without details could be distinguished against the obliterating optical interference caused by the swellings, cracks, and ruptures.

Example 3

In this example, an electrically conducting layer of chromium was evaporated on the supporting base member of polycarbonate resin film to a thickness of about 60 A. The above-described thermosetting phenolic polymer in the butyl cellosolve solvent was applied to give about a 1 micron thick coating over the chromium layer and then the tape was heated for one hour at approximately 75° C. to effect conversion of the phenolic polymer to the thermoset stage. A layer of the thermoplastic polymer 8 microns thick was applied to the phenolic polymer surface employing the same solution as was used in the preceding examples. Examination of the tape thus prepared showed that there was neither swelling nor cracking of either the chromium layer or of the polycarbonate resin layer, nor was the chromium layer ruptured. When this tape was projected and view in a dark field optical system in the same manner as above, the recorded signal was completely free of any optical interference caused by solvent-produced swellings, cracks, or ruptures.

Example 4

An electrically conducting 600 A. thick layer of indium oxide was applied to the polycarbonate resin film by depositing on a supporting polycarbonate resin indium and oxygen simultaneously and then heating to form the indium oxide layer. A layer of thermoplastic polymer eight microns thick was applied to the indium oxide layer from the above-mentioned thermoplastic polymer solution. After evaporation of the solvent, it was found that the tape showed extensive swelling and cracking caused by the solvent used with the thermoplastic polymer. However, by coating the polycarbonate resin film and the indium oxide coating with the above-described phenolic resin prior to applying the thermoplastic layer, the above-described swelling and cracking were completely elimi-

nated, and even under microscopic examination showed no evidence that there was any damage to either the conducting layer or the polycarbonate layer. This latter tape could be projected and viewed in a dark field optical system without any evidence of optical interference caused by any swellings, cracks, or ruptures ordinarily found as a result of the solvent contact.

From the above results, it will be clearly apparent that by means of the barrier, non-gas-releasing thermoset layer applied to either the polycarbonate resin film itself or to the polycarbonate resin film in combination with the conducting layer, it is possible to avoid damage to the polycarbonate resin film and to give recording media for the thermoplastic recording and read-out which are clear and unaffected by solvents which may be used in depositing the thermoplastic polymer on the surface of the conducting layer. By employing the barrier, non-gas-releasing polymer on the conducting metallic or metal compound layer, it is also possible to reduce the tendency to oxidation of the conducting layer, which is prone to oxidation, even at the moderately elevated temperatures which are ordinarily employed for either curing the barrier polymer or for "fusing" the charges which are introduced in the thermoplastic layer by electron bombardment. This is an extremely desirable feature of the invention because oxidation of the conducting inner layer alters the electrical properties of this member, thus undesirably modifying the heating characteristics and electrostatic charge transfer characteristics of the recording medium.

The interaction or chemical reaction above-described is generally aggravated by re-use of the recording medium. Thus, the re-use of recording medium bearing the information deformations first requires erasure of the deformations which can be achieved simply by heating the recording layer above the liquid point of the thermoplastic material. The recording medium is reheated each time it is desired to erase the previously recorded information or to record new information and repeated heating generally results in more pronounced interaction between the recording layer and the substrate, or a chemical reaction between a member of the recording medium and the external surroundings. It is therefore desirable to stabilize the recording medium so as to preserve the integrity of the composite member against both internal and external influences.

A still further advantage derived from the practice of my invention involves the discovery that by employing these thermoset non-gas-releasing polymers, it is possible to apply a conducting layer to the surface of the thermoset polymer to obtain an adhesion which is in many instances better than the adhesion of the conducting layer directly to the polycarbonate resin layer.

The following examples illustrate the use of other types of thermosetting non-gas-releasing polymers which can be employed to protect the polycarbonate resin from the effects of solvents and other environments which adversely affect the polycarbonate resin, while at the same time forming a strong bond between the polycarbonate resin surface and the applied film of the thermosetting polymer. In each of the following instances, a solution of the coating polymer in a specified solvent was applied by dipping film samples of the polycarbonate resin (employed in the previous examples) in the solution, air-drying for a short period of time to remove volatile solvent, and then heating at elevated temperatures for a time sufficient to effect cure of the thermosetting polymer. Thereafter, benzene and acetone were each placed on the coated film to measure the solvent resistance of the coated polycarbonate resin film. If no cracking, rupturing, or crazing of the polycarbonate film occurred, it was considered that the barrier layer of the thermosetting polymer was sufficiently effective to protect the polycarbonate resin from the adverse effects of the benzene and acetone. In the following examples, all percentages are by weight.

Example 5

Polycarbonate film was coated on each side with a film about 1–15 microns thick of a phenol-formaldehyde resin dissolved in a mixture of ethyl alcohol and butyl Cellosolve to a solids content of about 30%. After heating the coated film for 24 hours at 150° C., the film was examined and found to be substantially free of optical defects when projected by dark field optics (where only scattered light is being viewed). When benzene and acetone were placed on the film to measure the solvent resistance, the optical quality and the solvent resistance were observed to be unchanged as contrasted to the untreated polycarbonate film which crazed under the same test and became optically distorted and unacceptable. When the phenolic resin solution was combined with ethyl alcohol and diacetone alcohol as the solvents so that the phenolic resin was present in a solids weight content of about 25%, and the polycarbonate resin was dipped in the phenolic resin solution and coated with a film about 1–15 microns thick and thereafter heated for 24 hours at 150° C., the composite film was optically clear of defects when evaluated in a dark field projector. Benzene and acetone when placed on the film exercised no adverse solvent effect on the film. The same results were obtained when a 50% ethyl alcohol solution of the same resin was dissolved in equal weight proportion in a mixture of solvents comprising 50% toluene, 20% secondary butyl acetate, 10% isopropyl acetate, 10% isopropyl alcohol, 5% Cellosolve and 5% Cellosolve acetate, and the treated polycarbonate film was cured for 24 hours at 150° C.

Example 6

In this example, a phenol-formaldehyde resin was dissolved to 25% solids content in a solvent of 25% ethyl alcohol and 50% benzene. Polycarbonate film was dipped in this solution and after curing for 24 hours at 150° C., the film was examined for optical defects in a dark field projector. No defects were found in the film and even subjecting the film to the action of benzene and acetone caused on deleterious effects, showing the film to be completely resistant to the cracking and crazing influence of the benzene and acetone. That it was possible to use a benzene solution with a phenolic resin was entirely unexpected and in no way could have been predicted because previously it would have been suspected that the presence of the benzene would cause undesirable changes in the polycarbonate resin film. However, due to the modifying and moderating action of the phenolic resin, the benzene solvent caused no harmful effects on the polycarbonate resin film.

Example 7

Polycarbonate resin film was coated on both sides to a thickness of about 1 to 15 microns, with a phenolic resin comprising a condensation product of para-tertiary-amylphenol and formaldehyde dissolved in bodied soya oil and petroleum spirits to a solids content of about 50%. After heating for 24 hours at 150° C. to convert the phenolic resin to the thermoset state, the film was examined for optical defects and found to be substantially free of such defects. This protected film was found to be completely resistant to attack by benzene and acetone placed on the film. The same results were obtained by employing the same phenolic resin in combination with either butyl Cellosolve as the solvent or diacetone alcohol as the solvent.

Example 8

A methyl phenyl polysiloxane resin was made from a methyl phenyl polysiloxane containing an average of about 1.2 to 1.5 total methyl and phenyl groups per silicon atom wherein the phenyl to methyl ratio was about 60 to 40. A methyl phenylpolysiloxane resin having an

average of about 1.4 total methyl and phenyl groups per silicon atom and containing monomethylsiloxy units, monophenylsiloxy units, dimethylsiloxy units, and diphenylsiloxyl units was dissolved to a solids count of 60% in xylene. Polycarbonate resin film was dipped in the polysiloxane resin solution and heated for 24 hours at 150° C. to give a coated film which was optically clear and which was resistant to the effects of benzene and acetone applied to the surface of the film. The same results were obtained by using the methyl phenyl polysiloxane resin in the form of a 50% solids solution in butyl Cellosolve, or using as the solvent a mixture of cersol and diacetone alcohol. Even when the solution for the methyl phenylpolysiloxane resin was a mixture of toluene, secondary butyl acetate, isopropyl acetate, isopropyl alcohol, Cellosolve and Cellosolve acetate, and this solution of the methyl phenylpolysiloxane was applied to polycarbonate film there were no apparent optical defects in the treated film nor did benzene or acetone exert any adverse effects when placed in contact with the coated film.

Example 9

In this example, a 50% solids solution of a methylpolysiloxane resin containing an average of about 1.2–1.4 methyl groups per silicon atom, dissolved in butyl Cellosolve was applied to a thickness of between 1 to 15 microns on the polycarbonate resin film and thereafter heated for 24 hours at 150° C. to effect cure of the methylpolysiloxane resin. Examination of the treated films showed no evidence of any optical interference and the treated film was resistant to benzene and toluene when the latter were brought in contact with the treated film. Even when one employed a mixture of xylene and naphtha as the solvent for the methylpolysiloxane in place of the butyl Cellosolve, and this solution was applied to the polycarbonate resin film and cured, no optical interference or other deleterious effects were noted, and again the benzene and acetone when placed on the film failed to exert any harmful effects.

Example 10

In this example a heat-bodied methyl phenylpolysiloxane resin dissolved to a 60% weight solids content in toluene and containing an average of about 1.2 to 1.4 total methyl and phenyl groups per silicon atom, where the phenyl-to-methyl ratio was about 40 to 60, was then formed into a more dilute solution by combining 25 weight percent of the polysiloxane resin solution with 75 weight percent of a mixture on a weight basis of 50% toluene, 20% secondary butyl acetate, 10% isopropyl acetate, 10% isopropyl alcohol, 5% Cellosolve and 5% Cellosolve acetate. The polycarbonate resin film was dipped in this solution and heated for 24 hours at 150° C. to cure the polysiloxane and to give a film which was free of optical defects. Again, neither benzene nor acetone, when placed on the surface of the film in any way affected the ability of the coating on the polycarbonate resin film to resist the action of these solvents.

Example 11

In this example, an aromatic polyester was made from a mixture of ingredients comprising hydroquinone diacetate, isophthalic acid, and diphenic acid, in accordance with the procedure described in the application of Kantor et al., Serial No. 33,124, filed June 1, 1960, and assigned to the same assignee as the present invention. A coating solution was made of this resin comprising on a weight basis 5% of the aromatic polyester resin, 45% cresol, and 50% xylene. This mixture of ingredients containing a cross-linking agent for the aromatic polyester resin was then applied to the surface of the polycarbonate resin film to a thickness of about 1 to 15 microns and heated for about 24 hours at 150° C. Examination of the film in a dark field projector revealed that there were no interfering optical defects on the surface of the film. Furthermore, it was found that even though benzene and acetone were placed on the film, no attack occurred of either the surface of the aromatic polyester or of the polycarbonate resin.

It will be noted from the above examples that even though the polycarbonate resin was immersed in solutions of the coating resins where the solvent might be expected to adversely affect the polycarbonate resin, the concomitant presence of the film-forming thermosetting resin on the polycarbonate resin served to moderate the action of the solvent on the polycarbonate resin and actually imparted improved results. This is believed caused by the fact that there was sufficient solvent action by the coating polymer solvent to soften and swell the surface of the polycarbonate resin. Particularly, the sharp edges of surface defects, scratches, etc., swelled and become rounded by the action of the solvent. Thereafter, it is believed that the thermosetting coating was able to intermingle sufficiently with the swollen surface so that surprisingly the swelled surfaces were unable to return to their original sharp edge state after the solvent evaporated. With the sharp edges removed by being rounded off from the solvent action and from the action of the coating polymer, the excessive scattering of light during dark field projection was reduced to acceptable minimum levels. This effect has been unobtainable when no polycarbonate surface swelling solvent was employed or when the coating resin was incompatible with the polycarbonate resin. The solvent resistance of the coated polycarbonate resin becomes essentially the same as that of the coating polymer. Furthermore, there is no critical problem of matching the refractive index of the polycarbonate resin as long as the coating polymer is transparent.

The class of useful thermoset polymers also includes other cross-linkable (i.e., curable) resin systems including some polyepoxides (known as epoxy resins) containing amine or anhydride curing agents, and heat-curable (e.g., by peroxides) unsaturated polyesters containing copolymerizable monomers such as styrene and diethylene glycol maleate, styrene and diallyl phthalate, etc.

It will, of course, be also apparent to those skilled in the art that the present invention is not limited to the disposition of a single thermoset layer between the base polycarbonate layer and the recording layer, but also is intended to include those cases where the thermoset layer by virtue of its presence on the backside, that is, the underside of the polycarbonate resin layer furthest from the thermoplastic layer, improves the non-adhesive characteristic of the polycarbonate resin layer either to itself or to the thermoplastic layer in those cases where the recording medium is a tape which is wound into a reel upon itself and, therefore, will bring into contact surfaces composed of unlike compositions.

In addition to the above-described coating resins and polymers on the polycarbonate resin and the above-described conducting coatings and thermoplastic polymer, other materials may be employed in their place, many examples which have been given above and in the above-described Boldebuck and Glenn applications, without departing from the scope of the invention. The proportions of ingredients, the solvents, etc., can also be varied, subject to the precautions mentioned above.

In addition to the use of polycarbonate resins coated with the barrier, non-gas-releasing film-forming polymer for recording media, the coated polycarbonate resin can also be used in other applications where the latter may come in contact with solvents which tend to craze or crack or otherwise adversely affect the polycarbonate resin. Among such instances are those cases where molded parts, such as for instance, light reflectors, light shields, or even electrical conductors insulated with polycarbonate resins may encounter solvents harmful to the polycarbonate resin. These harmful effects can be eliminated by

applying to the surface of the polycarbonate resin the barrier non-gas-releasing polymers recited above.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A recording medium comprising a layer of a thermoplastic polymer having a liquid temperature of at least 85° C., a supporting base layer comprising a polycarbonate resin, a conducting layer intermediate the base layer and the thermoplastic polymer layer, and an inner layer of a non-gas-releasing, film forming, thermoset polymer interposed between the thermoplastic polymer layer and the supporting base layer.

2. A recording medium comprising a supporting polycarbonate base resin layer, an outer thermoplastic polymer layer having a liquid temperature of at least 85° C., a thermoset, non-gas-releasing, continuous coating on the polycarbonate resin layer, and an intermediate conducting layer between the thermoset non-gas-releasing polymer and the thermoplastic polymer layer.

3. A recording medium comprising a polycarbonate base resin layer, an outer thermoplastic polymer layer having a liquid temperature of at least 85° C., an intermediate conducting layer directly superposed on the polycarbonate resin layer, and a non-gas-releasing thermoset continuous resin coating interposed between the conducting layer and the thermoplastic polymer layer.

4. A recording medium as in claim 3 in which the polycarbonate resin layer has an additional continuous coating of the thermoset, non-gas-releasing polymer on the under side of the polycarbonate resin layer furthest from the thermoplastic layer.

5. An optically clear recording medium which comprises a recording layer of a thermoplastic polymer having a liquid temperature of at least 85° C., a base supporting layer comprising a polycarbonate resin, a conducting layer comprising chromium, and an intermediate barrier layer comprising a thermoset phenol-aldehyde resin between the polycarbonate resin layer and the thermoplastic layer.

6. An optically clear recording medium which comprises a recording layer of a thermoplastic polymer having a liquid temperature of at least 85° C., a base layer comprising a polycarbonate resin, a conducting layer comprising chromium, and an intermediate barrier layer comprising a thermoset phenol-formaldehyde resin between the polycarbonate resin layer and the conducting layer.

7. An optically clear recording medium which comprises a recording layer of a thermoplastic polymer having a liquid temperature of at least 85° C., a base layer comprising a polycarbonate resin, a conducting layer comprising chromium, and an intermediate barrier layer comprising a thermoset organopolysiloxane resin between the polycarbonate resin layer and the conducting layer.

8. An optically clear recording medium which comprises a recording layer of a thermoplastic polymer having a liquid temperature of at least 85° C., a base layer comprising a polycarbonate resin, a conducting layer comprising chromium, and an intermediate barrier layer comprising a thermoset hydroquinoneisophthalate resin between the polycarbonate resin layer and the conducting layer.

9. An optically clear recording medium which comprises a recording layer of a thermoplastic polymer having a liquid temperature of at least 85° C., a base layer comprising a polycarbonate resin, a conducting layer comprising indium oxide, and an intermediate barrier layer comprising a thermoset phenol-formaldehyde resin between the polycarbonate resin layer and the thermoplastic layer.

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