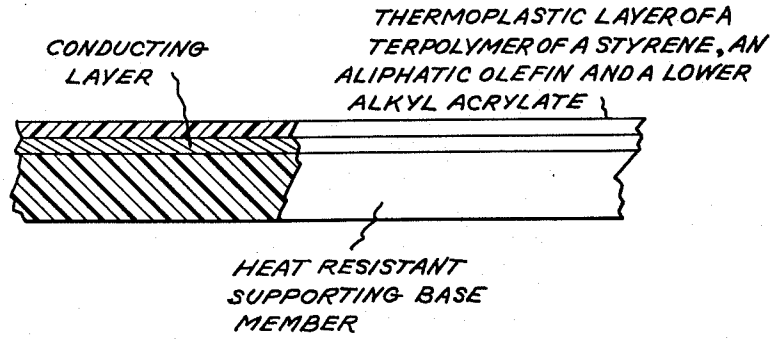
Jan. 21, 1964 A. KATCHMAN 3,118,787

RECORDING MEDIUM HAVING AN IMAGE RECEIVING COATING OF A TERPOLYMER OF A STYRENE, AN ALIPHATIC OLEFIN AND A LOWER ALKYL ACRYLATE

Filed Oct. 30, 1961



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United States Patent Office 3,118,787 Patented Jan. 21, 1964

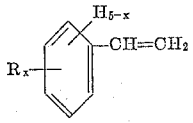
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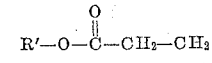
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Filed Oct. 30, 1961, Ser. No. 148,463
9 Claims. (Cl. 117—211)

This invention is concerned with compositions of matter and articles prepared therefrom useful in the recording, storing and reproducing of photographic images, technical data, etc. More particularly, the invention relates to a recording medium comprising a base supporting member and a thermoplastic layer thereon comprising a solid terpolymer of (*a*) from 10 to 20 mol percent of a member selected from the class consisting of isoprene, 2,3-dimethylbutadiene-1,3 and butadiene-1,3 (hereinafter collectively referred to as "aliphatic olefin"), (*b*) from 65 to 75 mol percent of a styrene (hereinafter so designated) of the formula



where R is selected from the class consisting of hydrogen, methoxy, and methyl radicals and x is a whole number equal to from 0 to 2, and (*c*) from 5 to 15 mol percent of an acrylate (hereinafter also so designated) having the formula



where R′ is a lower alkyl radical of from 1 to 4 carbon atoms (e.g., methyl, ethyl, propyl, butyl, isopropyl, isobutyl, etc.), the total molar concentration of the three ingredients used to make the terpolymer being equal to 100 mol percent. The recording media can be in the form of films, for instance, tapes, sheets, etc. as well as slides, disks, etc., which are suitable for recording, storing and reproducing photographic images and technical data, employing the above styrene-acrylate-aliphatic olefin terpolymer as the thermoplastic layer in which such images 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 of which are assigned to the same assignee as the present invention and are abandoned, 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 which 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 on the heat-deformable thermoplastic layer is then converted 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 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 the recording medium, the latter can also be employed as a "master copy" for duplication by techniques similar to phonograph disk stampings.

There are several requirements which are necessary for a satisfactory recording medium ("recording medium" or "recording material" will hereinafter be intended to mean the composite structure including the upper thermoplastic layer upon which the information is recorded and used in the electronic recording previously described, the base supporting layer and the conducting layer if it is part of the composite structure). In the first place, the recording medium must have optical clarity and must be transparent. It is preferably water-white (i.e., water-clear) or only slightly tinted in thin films. Any trace of haze should be avoided in the recording medium because it will interfere with the later "reading out" or projection of any images which may have been introduced into the recording medium.

The recording medium must also have certain electrical characteristics, particularly it must be a good insulator and have high electrical resistivity; usually it is desirable that the specific resistivity be greater than about 10^{11} ohm-centimeters when in the liquid state at the time it is heated to effect formation of any depressions or ridges or other deformations in the surface thermoplastic layer.

In addition, for certain applications, particularly in tapes, the recording medium, including the surface thermoplastic layer, must be sufficiently flexible and strong to enable it to be rolled up around small diameters especially when the thermoplastic layer is present in thicker than usual sections. These are the usual requirements encountered in the case of projection machines, for instance, 16-millimeter projection machines which may be used to project the image on the screen.

The thermoplastic layer of the recording medium must be stable under moderate electron bombardment from the electron high voltage accelerating apparatus. The thermoplastic layer preferably has a maximum vapor pressure of 10^{-5} to 10^{-6} mm. Hg when in the liquid state,

that is, when it is subjected to the elevated temperatures required to deform the thermoplastic layer of the recording medium in accordance with the changes thereon. The thermoplastic layer must also be stable at elevated temperatures at which it will be deformed by the heat necessary to "develop" the charge on the thermoplastic layer.

Of major importance, the thermoplastic layer of the recording medium must be capable of having a fairly sharp melting point in order that the developing of the proper image on the thermoplastic layer proceed with a minimum of control difficulties. For a broad spectrum of use, 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 about 85° C. depending on the supporting backing layer.

Since the recording medium may comprise at least two layers and more often three layers, it is also essential that the thermoplastic layer have good adhesion to the backing material, whether it is the supporting backing or the conducting layer. Since one embodiment of the recording medium comprises a three-layer structure composed of the backing material, the upper surface thermoplastic layer and an intermediate conducting layer (for instance, a thin film of metal, or a metal oxide, or a metal salt), it is additionally important that the thermoplastic layer have good adhesion to the conducting layer or the conducting surface.

As a further requirement, it is important in those cases where the recording medium will be in the form of a tape and thus will be rolled upon itself and stored, that the thermoplastic layer be substantially free of cold flow that will cause any change in the configuration of the recorded information on the thermoplastic surface, such as any depressions or hills or other deformations on the surface of the thermoplastic layer. Since the storage might take place under conditions where the temperature might rise to as high as 40° C. to 50° C., this cold flow must be nonexistent or very low even at these temperatures. Any significant cold flow may render the tape incapable of storage in reel condition as is the usual movie film. As a still further requirement, it is essential that the thermoplastic layer have good resistance towards oxygen attack so that it maintains high electrical resistivity during processing of the tape. Again, in those cases where a tape is involved, and because the tape may be rolled up on itself, it is also essential that the thermoplastic layer should be non-tacky and should not stick to itself or to any other surface with which it might come in contact in the rolled-up state.

Although thermoplastic compositions are described in the aforementioned pending applications of William E. Glenn, Jr., Serial Nos. 698,167 and 783,584, it has been found that these thermoplastic materials do not have a sharp enough fusion point to the liquid state of the thermoplastic layer; furthermore, there is much to be desired in the adhesion of the thermoplastic layer to the conducting layer. Additionally, it has been found that the thermoplastic layer should be more flexible in those instances where the recording medium would be wound around small diameters such as in the case of spindles and sprockets used in projection equipment. As a still further area of improvement, the thermoplastic layer should resist adhesion to the adjacent back of the base layer when the film is in the rolled-up state, for instance, as a reel, or a spool, etc.

A recording medium which employs a thermoplastic layer embracing the above-mentioned desirable characteristics is found described and claimed in the copending application of Edith M. Boldebuck, Serial No. 8,587, filed February 15, 1960, and assigned to the assignee of the present invention now U.S. Patent 3,063,872, issued November 13, 1962. In this Boldebuck application, the recording medium contains as the thermoplastic layer, a solid heat deformable mixture of ingredients comprising

(1) an organopolysiloxane and (2) a thermoplastic, solid (i.e., 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*). Although these thermoplastic compositions have been found to be useful and to possess improved properties over thermoplastic layers previously employed in the above-described recording media, nevertheless certain difficulties have arisen in connection with the use of these thermoplastic compositions for the recording medium.

In the first place, the Boldebuck thermoplastic layer is composed of a mechanical mixture of ingredients containing at least two preformed compositions, namely, the organopolysiloxane and and the aryl polymer. It is obvious that the use of two such materials for a thermoplastic composition introduces many control problems in preparing these compositions and insuring that the properties eand characteristics of each of the ingredients satisfies specifications designed to render the thermoplastic composition optimum for use as a thermoplastic layer. Furthermore, the compositions used for the thermoplastic layer in the Boldebuck recording medium are relatively expensive materials and add to the cost of the recording medium. In addition it has also been found that the thermoplastic composition used in the Boldebuck application has reduced flexibility when used in thicker sections so that the ability to bend films containing thicker sections of the Boldebuck compositions over small diameters, for instance, over ⅜ inch to ½ inch diameter mandrels is materially reduced. This is an undesirable characteristic when it is desired to use projection machines for recording medium tapes in which the sprockets carrying the film are extremely small. Finally, the means for making each of the polymeric elements comprising the Boldebuck thermoplastic layer requires extensive processing and careful control of the process, thus again adding to the cost of the ultimate recording medium.

Unexpectedly, I have discovered that in addition to the desired improvements for the thermoplastic layer which have been referred to above, I am also able to overcome the difficulties which have arisen in connection with the use of a thermoplastic recording medium composed of an organopolysiloxane and the aryl polymer, by employing as the thermoplastic layer a solid terpolymer of from 10 to 20 mol percent of the aliphatic olefin, 65 to 75 mol percent of the styrene, and from 5 to 15 mol percent of the acrylate, the total mol percents being equal to 100 mol percent. In addition to obviating the difficulties recited above, it has also been found that improvements are noted in the ability to coat the base members either with or without the conducting layer over that resulting from trying to coat the base member with previously known thermoplastic compositions for recording media of the type described above.

The discovery that this particular terpolymer of specific monomers in the specified proportions was useful in recording media and possessed improved properties over those heretofore described was entirely unexpected and in no way could it have been predicted for the reason that it might have been expected that the aliphatic olefins would cause residual unsaturation in the terpolymers thus resulting in cross-linking of the thermoplastic layer. Unexpectedly this did not occur and was believed due to the presence of the aromatic nuclei of the styrene. The use of proportions outside the above ranges resulted in a thermoplastic layer which had either poor adhesion to the conducting layer or reduced flexibility of the thermoplastic layer in thicker sections, e.g., in thickness of from 10 to 25 microns.

It is accordingly one of the objects of this invention to prepare a polymeric composition which can be used as a thermoplastic layer for recording, storing and reproducing photographic images, technical data, etc.

Another object of the invention is to prepare recording media in which the thermoplastic layer of such recording

media is prepared from a single composition rather than a mechanical mixture of ingredients.

It is a still further object of the invention to prepare recording media in which the thermoplastic layer thereon is sufficiently flexible so as to be capable of being wound around extremely small diameters even when in thick sections without cracking or in any way separating from the substrate to which it is applied.

An additional object of the invention is to prepare a recording medium in which the thermoplastic layer on which information will be recorded and stored will have no undesirable affinity for the base layer with which it may come in contact in a rolled-up state and will show no undesirable cold flow when subjected to the pressures which may be encountered in the case of film maintained for long periods of time in the rolled-up state.

Other objects of the invention will become more apparent from the discussion which follows.

Among the styrene compounds which may be employed in the practice of the present invention may be mentioned styrene, p-methyl styrene, p-methoxystyrene, 2,4-dimethyl styrene, 2,5-dimethyl styrene, etc.

Among the acrylates which may be used are methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, etc.

The thermoplastic composition used as the thermoplastic layer in our recording medium can be prepared by various means. For instance, one can mix together from 10 to 20 mol percent of the aliphatic olefin, from 65 to 75 mol percent of the styrene, and from 5 to 15 mol percent of the acrylate, add from about 0.1 to 2 percent, by weight, of a polymerization catalyst such as any of the organic peroxides or azo compounds (e.g., benzoyl peroxide, tertiary butyl perbenzoate, azobisisobutyronitrile, etc.), an inorganic peroxide (e.g., hydrogen peroxide, sodium peroxide, sodium perborate, etc.), and thereafter the mixture of ingredients is heated under polymerizing conditions, for instance, at temperatures of about 50 to 125° C. (either under atmospheric or super-atmospheric pressures) for times ranging from about 15 minutes to 3 to 4 hours or more until the desired molecular weight of the terpolymer is obtained. Thereafter the polymer is advantageously separated, for example, by precipitation from any low molecular materials or unreacted monomers by treating with an alcohol such as methanol. Further isolation of the polymer in the usual fashion is designed to give a thermoplastic composition which has a number average molecular weight within the range of from about 10,000 to 50,000 when measured at 25° C. by osmotic means using benzene as the solvent. Under many conditions of use, it is desirable that the thermoplastic terpolymer have a stick temperature of 65–90° C., a fluid temperature (i.e., becomes a fluid) of about 105–115° C., and when used on a recording tape have sufficient flexibility to be able to be wound around a mandrel as small as ⅜ (or even less) inch in diameter without cracking.

The backing material for the recording medium may be either a flexible composition or may be a rigid material. Examples of rigid materials which can be employed (keeping in mind that optical clarity, heat resistance, and radiation resistance are usually the required properties) are, for instance, glass (in the form of plates, slides, disks, etc.); unsaturated polyester resins (formed from the reaction of a polyhydric alcohol, such as ethylene glycol, diethyl glycol, propylene glycol, dipropylene glycol, etc., and an alpha-saturated alpha-beta-dicarboxylic acid or anhydride, for instance, maleic acid, maleic anhydride, fumaric acid, citraconic acid, etc.); combined with these unsaturated polyesters one may also incorporate such copolymerizable cross-linking ingredients, such as diallyl phthalate, diethylene glycol dimethacrylate, etc. One can also employ metals such as aluminum, nickel, chromium, etc., where the metal serves both as a conducting layer and as a reflective surface which can be read optically by reflection.

Examples of flexible materials which can advantageously be employed as the backing material are, for instance, polyethylene terephthalate (which can be obtained by the transesterification of esters of terephthalic acid with divalent alcohols, for example, ethylene glycol as shown in U.S. Patent 2,641,592—Hofrichter), such polyethylene terephthalate being sold by E. I. du Pont de Nemours and Company of Wilmington, Delaware, under the name of Mylar. A more refined grade of polyester terephthalic acid tape or film found highly appropriate as the basis for recording images (and which contains small intercondensed residues from dihydric alcohols, such as, propylene glycol-1,3 to reduce crystallinity) is sold under the name of "Cronar."

Another backing material which can be used advantageously because of its good heat resistance, strength, inertness and resistance to radiation are polycarbonate resins corresponding to the formula



where R_1 is hydrogen or a monovalent hydrocarbon radical, many examples of which have been given above for R (where more than one R_1 is used, they may be the same or different); R_2 is selected from the class consisting of alkylene and alkylidene residues (e.g., methylene, ethylene, propylene, propylidene, isopropylidene, cyclohexylidene, etc.), oxygen, etc.; C is the residue of an aromatic nucleus, (e.g., benzene, naphthalene, biphenyl, etc. nucleus); Y is a substituent 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 reaction conditions, *e* 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 C; *t* is a whole number equal to from 0 to a maximum determined by the number of replaceable nuclear hydrogens on R_2; and *w* is a whole number equal to from 0 to 1, inclusive. These compositions and directions for preparing these compositions are disclosed and claimed in the copending application of Daniel W. Fox, Serial No. 520,166, filed July 5, 1955, and assigned to the same assignee as the present invention. By reference, this application is made a part of the disclosures and teachings of the instant application. It will be apparent to those skilled in the art that other compositions may be employed as backing materials where the softening point is sufficiently high so as to allow heating of the thermoplastic layer without adversely affecting the base layer.

In many instances, there is interposed between the thermoplastic surface and the backing, a conducting layer which can be subjected to radio frequency energy as a means for heating the thermoplastic layer. This conducting layer acts as the layer which becomes positively charged beneath the thermoplastic layer and when the thermoplastic layer is heated to cause the thermoplastic material to become fluid and deformable, 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 (which should be thin enough to be optically clear if interposed between the base and the thermoplastic layer) 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, etc. In using the conducting layer, it is essential that the layer of metal or metal compound applied to the base layer be no thicker than is required to obtain a transparent film thereon. For this reason, it has been found that the metal film is advantageously of the order of about 10 to 100 angstroms (A.) or 0.001 to 0.01 micron thick, and that it should have a resistivity of between 1,000 and 10,000

ohms per square centimeter for optimum radio frequency heating if that is the method used for developing the deformation pattern.

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.; this base layer 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 backing by the well-known method of volatilizing the metal or metal compound in a vacuum at elevated temperatures and passing the backing 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 backing and preferably while the entire assembly is still under vacuum. One method for applying a metal salt conducting layer to the backing, e.g., polyethylene terephthalate, 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. 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.

In the accompanying drawing, the single figure shows a tape recording medium composed of an upper thermoplastic layer 1 comprising a copolymer of a styrene, an aliphatic olefin, and an acrylate within the molar proportions recited above, a base member 2 supporting the thermoplastic layer, and an intermediate conducting layer 3.

The following examples are given by way of illustration and not by way of limitation, as to how the present invention may be practiced. All parts and molar concentrations are by weight unless otherwise noted.

The "liquid temperature" of the thermoplastic compositions described below was determined by placing on a melting point block a sample of chromium-coated polyethylene terephthalate film (Cronar film), on which a film of the thermoplastic composition had been deposited and the solvent evaporated. The thermoplastic surface was scratched with a needle as the temperature was gradually raised, and the temperature at which the thermoplastic terpolymer flowed in immediately to obliterate the scratch was recorded as the "liquid temperature."

The intrinsic viscosities (which preferably are within the range of from 0.05 to 0.35 dl./g.) described below were obtained at 25°C. by using benzene as the solvent. The number average molecular weight was determined by osmotic pressure using benzene as the solvent. Finally, the "stick temperature" of the terpolymer was determined by heating the tape with the terpolymer composition on the surface and bringing the polyethylene terephthalate backing into contact with the heated terpolymer surface and determining the temperature at which the terpolymer stuck or caught on to the applied backing.

The actual writing on the thermoplastic surface (which was about 7–12 microns thick) was carried out as follows. An electron gun was mounted in an evacuated apparatus (described in the Glenn applications) containing an infrared heater. The optically clear tape was passed over the heater and while the thermoplastic layer was in the molten condition (as a result of heating the tape to a temperature of about 90–100° C.), it was exposed to the electron beam. The electron beam was controlled to sweep back and forth in a linear path as the tape was passed under the beam. While the beam was operated at a current of 1 microamp. with a 6 kv. accelerating potential drop from filament to ground plane (i.e., the conducting layer) about 1/60 of a second was required to inscribe information in an area of about 0.225 inch by 0.155 inch) for a single image by 262½ sweeps of the electron beam. The thermoplastic layer was then allowed to cool (while still in vacuum) to set or freeze the deformations in the surface of the thermoplastic layer.

Example 1

Into a pressure reactor were placed 7.5 parts azobisisobutyronitrile, 220 parts benzene, 43 parts (12.5 mol percent) methyl acrylate, 286 parts (68.75 mol percent) styrene, and 40.5 parts (18.75 mol percent) butadiene-1,3.

The reaction vessel was closed and polymerized with shaking at 75° C. for 10 hours. The polymer was precipitated from methanol and vacuum-dried to give 255 parts of a terpolymer having an intrinsic viscosity in benzene at 25° C. of 0.16 dl./g. and a number average molecular weight of 24,300. A 25 percent solution of this polymer in benzene was applied directly to about a 0.001 micron thick chromium-coated surface deposited on a 30 mm. wide by 0.004 inch thick optical grade clear polyethylene terephthalate tape sold as Cronar by E. I. du Pont de Nemours and Company (methods for preparing such film may be found disclosed in such patents as U.S. 2,678,285 and 2,698,241). After removal of the solvent by first air-drying and then by heating for 10 to 15 minutes at about 140–150° C., it was found that the copolymer layer was about 8–9 microns thick.

Testing of the above coated transparent optically clear recording medium for adhesion and flexibility of the thermoplastic layer to the metal conducting layer revealed that bending of the film around a mandrel ¼ inch in diameter caused no separation of the thermoplastic layer from the chromium coating nor was there any cracking of the thermoplastic layer. The thermoplastic layer had a fluid temperature of about 95–100° C. and a stick temperature of 68° C. The recording medium of Example 1, when written upon in the manner described above and in the Glenn applications, and when projected gave clear, well-defined images.

Example 2

In this example 57.2 parts (68.75 mol percent) styrene, 10.4 parts (18.75 mol percent) isoprene, 8.6 parts (12.5 mol percent) methyl acrylate, 1.5 parts azobisisobutyronitrile and about 44 parts benzene were charged to a reaction vessel similarly as was done in Example 1 and the reaction mixture subjected to polymerization conditions for 9 hours at 75° C. The polymer was precipitated in the same manner as was done in Example 1 with methanol to yield 39 parts polymer having an intrinsic viscosity of 0.12 dl./g. A benzene solution of this polymer was then deposited on a chromium-coated polyethylene terephthalate employing the same procedure as used in Example 1 to make an optically clear recording medium with the above-mentioned terpolymer as the thermoplastic layer. This tape could be bent around a mandrel ¼ inch diameter without any separation of the thermoplastic layer from the chromium coating and without any cracking or crazing of the thermoplastic layer. The thermoplastic terpolymer layer, which was about 7.5 microns thick, had a stick temperature of about 70° C. and a fluid temperature of about 100° C. The recording medium in this example could be written upon in the manner described in the aforesaid Glenn applications and when projected gave clear, well-defined images.

Example 3

In this example 57.2 parts styrene (68.75 mol percent), 8.1 parts (18.75 mol percent) butadiene-1,3, 10 parts (12.5 mol percent) ethyl acrylate, 1.5 parts azobisisobutyronitrile and about 40 parts benzene were placed in a reaction vessel and polymerized similarly as was done in Example 2 employing the same condition as therein described to give, after precipitation, about 42 parts of a

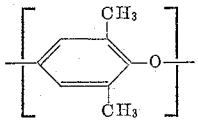
terpolymer having an intrinsic viscosity of 0.16 dl./g. When this thermoplastic terpolymer was applied to a chromium-coated polyethylene terephthalate film similarly as was done in the above examples to a thickness of about 7.5 microns, it was found that this thermoplastic terpolymer had a stick temperature of 65° C., a fluid temperature of 95° C., and could be bent around a ¼ inch diameter mandrel without any cracking or crazing of the surface. This optically clear recording medium could be written upon in the manner described in the foregoing Glenn applications and when projected gave clear, well-defined sharp images.

Example 4

This example illustrates the effect of using methyl methacrylate instead of, for instance, methyl acrylate, in making the thermoplastic terpolymer which is deposited on the recording medium. More particularly 57.2 parts (68.75 mol percent) styrene, 8.1 parts (18.75 mol percent) butadiene-1,3, 10.1 parts (12.5 mol percent) methyl methacrylate, 1.5 parts azobisisobutyronitrile, and about 44 parts benzene were subjected to polymerizing conditions similarly as was done in Examples 2 and 3 employing a time of 9 hours at temperature of 75° C. After precipitation there was obtained 48 parts of a terpolymer having an intrinsic viscosity of 0.12 dl./g. When this terpolymer (to a thickness of 7.5 microns) was applied to a chromium-coated polyethylene terephthalate film similarly as was done in the preceding examples, the thermoplastic terpolymer coating crazed when bent around a mandrel 1 inch in diameter, despite the fact that the stick temperature of the thermoplastic layer was 75° C. and the fluid temperature 105° C.

Example 5

In this example, on a weight basis, 90 percent of a diphenyl silicone, and 10 percent of a dimethyl phenylene ether polymer having recurring units of the formula



(these ingredients being prepared in accordance with the directions described in the aforementioned Boldebuck application) were intimately mixed together in a toluene solvent. A sample of this solution in about a 25 weight percent concentration was applied to a chromium-coated polyethylene terephthalate film to a thickness of about 8 to 10 microns, and the coating dried. Attempts to bend this film around a ¾ to 1 inch diameter mandrel resulted in cracking of the film. The film crazed on a 1-inch mandrel. As the thickness of the thermoplastic layer (composed of the two ingredients) increased, and the diameters of mandrels around which the tape could be bent without cracking or other evidence of deterioration were greatly increased.

It will of course be apparent to those skilled in the art that in place of the styrene, methyl acrylate, ethyl acrylate, butadiene-1,3, isoprene used in the previous examples, one can employ other styrenes, acrylates, and aliphatic olefins, many examples of which have been given above, without departing from the scope of the invention. In addition, the proportions of the ingredients can be varied within fairly wide limits consistent with the maximum and minimum ranges recited above.

It will also be apparent that where there is substitution on the nucleus of the styrene compound used for copolymerization with acrylate aliphatic olefin, the substitution can be in any positions, for instance, ortho, meta or para; where there is more than one substitution, the substitutions can be in the vicinal or avicinal (symmetrical, asymmetrical, etc.) positions. The sole precaution to be observed in such instances is that the position of the substituent on the benzene ring is such that it will not adversely affect the polymerization of the monomers undergoing copolymerization nor should it adversely affect attainment of the desired molecular weight which is required for obtaining the optimum properties of the thermoplastic coating when deposited on the substrate or on the metal or otherwise coated substrate.

Various modifying agents which do not adversely affect the properties required for the thermoplastic recording medium can be employed as, for instance, various plasticizers to raise or lower the liquid melting point of the thermoplastic layer, etc. In place of the polyethylene terephthalate other backings can be employed as, for instance, the polycarbonate resins heretofore recited.

The thermoplastic compositions and tapes made therewith can be employed in various applications and are particularly useful for recording of computer information. In addition, they can be used in the movie film industry whereby these tapes can be used to record the action being filmed and the image can be processed immediately after the action has been recorded on the film and by suitable optical apparatus transferred and projected to determine whether the action which was taken with the film is acceptable and satisfactory for final showing.

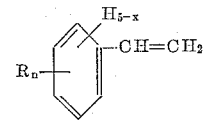
Additional directions for using recording media of the type described in the instant application can be found in the copending application of William E. Glenn, Jr., Serial No. 8,842, filed February 5, 1960, and assigned to the same assignee as the present invention.

Instead of heating the tape in the irradiation apparatus as was done in the preceding examples, the electron recorded information can be "developed" by outside heat treatment. One method comprises applying a current or blast of hot air to the surface of the charged thermoplastic layer where the temperature of the air is sufficiently high to effect liquefaction of the thermoplastic layer to the desired degree of flowability to cause the deformation on the surface thereof; another method comprises using radio frequency heating to arrive at the proper temperature for causing deformation of the surface of the thermoplastic layer; and finally, particularly when a tape is employed, the tape is passed over a heated drum maintained at the proper temperature wherein the surface of the base member furthest from the thermoplastic layer is in direct contact with the heated drum so that heat diffuses upward through the tape to the thermoplastic layer to cause the above-mentioned fusion and flowability of the latter.

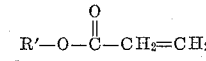
The polyethylene terephthalate tape employed in the preceding examples and the methods for manufacturing this particular tape are more particularly disclosed in U.S. Patents 2,465,319—Whinfield et al., issued March 22, 1949, and 2,779,684—Alles, issued January 29, 1957. The latter Patent 2,779,684 recites in greater detail the processing of polyethylene terephthalate film employed in the manufacture of the aforesaid Cronar.

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

1. A recording film consisting essentially of a flexible base supporting member and a thermoplastic layer composed essentially of a solid terpolymer of (*a*) of from 10 to 20 mol percent of a member selected from a class consisting of isoprene, 2,3-dimethylbutadiene-1,3, and butadiene-1,3, (*b*) from 65 to 75 mol percent of a styrene having the formula

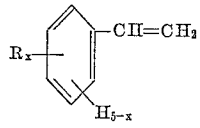


where R is selected from the class consisting of hydrogen, methoxy, and methyl radicals and *x* is a whole number equal to from 0 to 2, and (*c*) from 5 to 15 mol percent of an acrylate having the formula

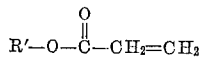


where R′ is a lower alkyl radical of from 1 to 4 carbon atoms.

2. An optically clear recording film consisting essentially of (1) a flexible transparent base supporting member, (2) a thermoplastic layer composed essentially of a solid terpolymer of (*a*) from 10 to 20 mol percent of a member selected from a class consisting of isoprene, 2,3-dimethylbutadiene-1,3, and butadiene-1,3, (*b*) from 65 to 75 mol percent of a styrene having the formula



where R is a member selected from the class consisting of hydrogen, methyl and methoxy, and *x* is a whole number equal to from 0 to 2 and (*c*) from 5 to 15 mol percent of an acrylate having the formula



where R′ is a lower alkyl radical of from 1 to 4 carbon atoms, and (3) an intermediate transparent conducting layer between the base member and the thermoplastic layer.

3. An optically clear recording film consisting essentially of (1) a flexible transparent supporting base member, (2) a thermoplastic layer composed essentially of a terpolymer of (*a*) from 10 to 20 mol percent butadiene-1,3, (*b*) from 65 to 75 mol percent styrene, and (*c*) from 5 to 15 mol percent methyl acrylate, and (3) an intermediate transparent conducting layer between the base member and the thermoplastic layer.

4. An optically clear recording film consisting essentially of (1) a flexible transparent supporting base member, (2) a thermoplastic layer composed essentially of a terpolymer of (*a*) from 10 to 20 mol percent isoprene, (*b*) from 65 to 75 mol percent styrene, and (*c*) from 5 to 15 mol percent methyl acrylate, and (3) an intermediate transparent conducting layer between the base member and the thermoplastic layer.

5. An optically clear recording film consisting essentially of (1) a flexible transparent supporting base member, (2) a thermoplastic layer composed essentially of a terpolymer of (*a*) from 10 to 20 mol percent isoprene, (*b*) from 65 to 75 mol percent styrene, and (*c*) from 5 to 15 mol percent ethyl acrylate, and (3) an intermediate transparent conducting layer between the base member and the thermoplastic layer.

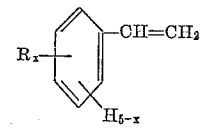
6. An optically clear recording medium consisting essentially of (1) a transparent polyethylene terephthalate supporting base member, (2) an outer thermoplastic layer

composed essentially of a terpolymer of (*a*) from 10 to 20 mol percent butadiene-1,3, (*b*) from 65 to 75 mol percent styrene, and (*c*) from 5 to 15 mol percent methyl acrylate, and (3) an intermediate transparent conducting layer comprising chromium.

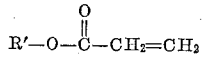
7. An optically clear recording medium consisting essentially of (1) a transparent polyethylene terephthalate supporting base member, (2) an outer thermoplastic layer composed essentially of a terpolymer of (*a*) from 10 to 20 mol percent isoprene, (*b*) from 65 to 75 mol percent styrene, and (*c*) from 5 to 15 mol percent methyl acrylate, and (3) an intermediate transparent conducting layer comprising chromium.

8. An optically clear recording medium consisting essentially of (1) a transparent polyethylene terephthalate supporting base member, (2) an outer thermoplastic layer composed essentially of a terpolymer of (*a*) from 10 to 20 mol percent isoprene, (*b*) from 65 to 75 mol percent styrene, and (*c*) from 5 to 15 mol percent ethyl acrylate, and (3) an intermediate transparent conducting layer comprising chromium.

9. An optically clear recording medium consisting essentially of (1) a transparent polycarbonate resin base supporting member, (2) a thermoplastic layer composed essentially of solid terpolymer of (*a*) from 10 to 20 mol percent of a member selected from a class consisting of isoprene, 2,3-dimethylbutadiene-1,3, and butadiene-1,3, (*b*) from 65 to 75 mol percent of a styrene having the formula



where R is a member selected from the class consisting of hydrogen, methyl and methoxy, and *x* is a whole number equal to from 0 to 2 and (*c*) from 5 to 15 mol percent of an acrylate having the formula



where R′ is a lower alkyl radical of from 1 to 4 carbon atoms, and (3) an intermediate transparent conducting layer between the base member and the thermoplastic layer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,492,124	Young et al.	Dec. 20, 1949
2,917,407	Walters et al.	Dec. 15, 1959
2,985,866	Norton	May 23, 1961