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Newman et al.

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[54] PROCESS OF MAKING PRESSURE-SENSITIVE TRANSFER ELEMENTS

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[52] **U.S. Cl.** .....**117/36.1**, 117/235, 117/155 UA, 117/138.8 F

[51] **Int. Cl.**.....**B41m 5/10**

[58] **Field of Search**.....117/36.1, 36.2

[56] **References Cited**

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[57] **ABSTRACT**

Preparation of pressure-sensitive transfer sheets based upon synthetic resinous film-forming binder materials in the absence of volatile solvents which comprises mixing a liquid polymerizable acrylic ester monomer, ink paste comprising oily material and colorant, and a polymerization catalyst, applying the composition as a thin layer and heating in an inert atmosphere to induce polymerization of said monomer to form a solid pressure-sensitive transfer layer.

7 Claims, 1 Drawing Figure

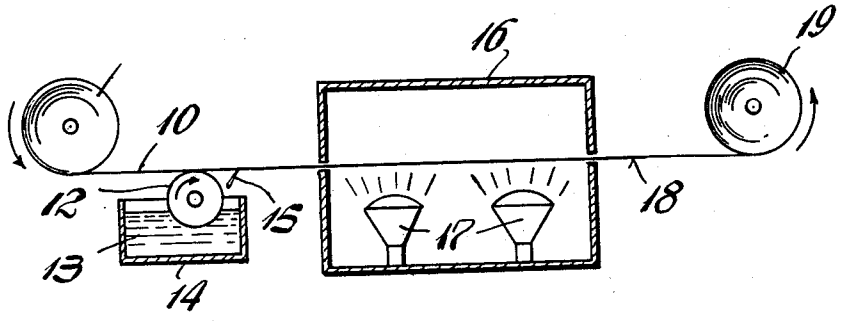


Fig. 1

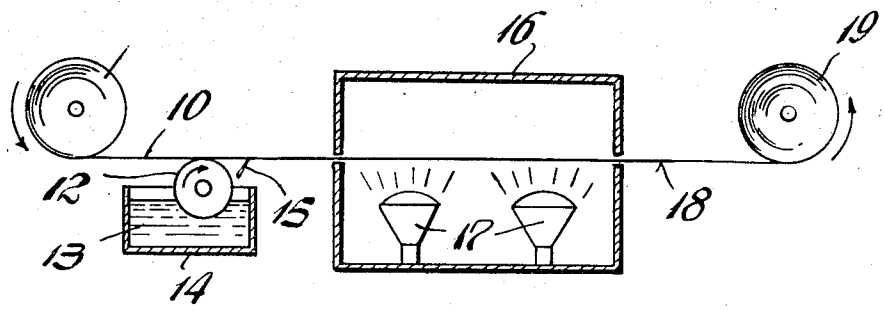
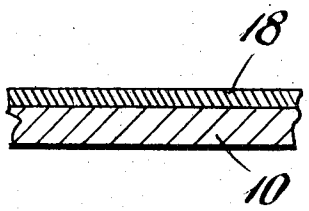


Fig. 2



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PROCESS OF MAKING PRESSURE-SENSITIVE TRANSFER ELEMENTS

This invention relates to the field of transfer sheets and ribbons of the so-called carbon paper type and more particularly to such sheets and ribbons in which the transfer layer is based upon a resinous binder material in place of the more conventional wax. Transfer elements of this type fall into two categories. The first type is the frangible transfer layer which transfers in mass or in toto under the effects of imaging pressure to form images which contain all of the ingredients of the transfer layer. Such transfer layers are most important for the imaging of hectograph master sheets and magnetic record sheets since a heavy physical deposit is important for the production of many spirit copies from a hectograph master and for the accurate sensing of a magnetic imaged record sheet.

The second type of resinous transfer layer is the so-called squeeze-out layer in which the resinous binder material is incompatible with the ink contained therein so that only the ink is squeezed out and transferred to the copy sheet under the effects of imaging pressure. Sheets of this type are reusable many times and are preferred for normal copy work because the formed images are clean and smear-resistant.

Resinous transfer elements of these types are well known in the art as illustrated by U.S. Pat. Nos. 2,984,582; 3,037,879; 3,054,692 and 3,177,086, among others. One of the greatest problems faced in connection with the production of such transfer elements is the hazard and expense of using the large amounts of volatile organic solvents required for such production. Such solvents are highly flammable and explosive and the vapors of some are highly toxic. Also, although these solvents are relatively expensive in the amounts wasted, the cost of recovering and purifying the solvents renders recovery impractical.

Attempts to avoid the necessity of using volatile organic solvents by using liquid monomeric starting materials have not proven to be commercially satisfactory up to the present because of the length of time required to polymerize the monomers and the difficulty in uniformly obtaining final solidified layers having the required pressure-sensitivity and transfer properties.

The present invention is concerned with overcoming the problems encountered during the formation of resinous transfer elements from monomers in the absence of volatile solvents and with providing anew and improved method for producing such transfer elements.

In the drawings:

FIG. 1 is a plan view illustration of an apparatus for carrying out the present process, and

FIG. 2 is a diagrammatic cross-section, to an enlarged scale, of a pressure-sensitive transfer element produced according to the present invention.

According to the present invention, we have discovered that pressure-sensitive transfer elements can be produced in a reliable, efficient and safe manner through the use of a particular class of polymerizable acrylic ester monomers, alone or in combination with low molecular weight polymers which are liquid or are soluble in the monomers used, polymerization being effected in an inert atmosphere under the effects of applied heat and in the presence of a polymerization catalyst. Polymerization will not occur in a satisfactory manner in the presence of oxygen gas or in the presence of air or other gas containing free, uncombined oxygen.

The monomers used according to the invention are acrylic ester monomers, alone or in combination with other polymerizable monomers or low molecular weight polymers, said acrylic monomer comprising at least about 30 percent by weight of the total binder material. The acrylic ester monomers useful according to the invention are the aliphatic esters of acrylic and methacrylic acid in which the aliphatic ester radical is substituted or unsubstituted and contains from one to five carbon atoms in the aliphatic chain. Preferred materials are hydroxyethyl methacrylate, hydroxyethyl acrylate, methyl methacrylate and butyl methacrylate.

The compositions of the present invention also comprise oleaginous material such as oils and/or waxy materials and colorants such as dyes and pigments. Fillers may also be included, particularly in connection with the production of frangible transfer layers where high amounts of filler assist in producing brittle, frangible coatings.

According to one embodiment of the invention, at least about 10 percent by weight of a low molecular weight synthetic thermoplastic polymer is included, based upon the total final resin content, to cause the monomer to polymerize more rapidly so that hardening or drying of the transfer layer occurs in a shorter period of time than possible when the monomer is used alone. The liquid monomer functions as a solvent or diluent for the polymer and as a dispersion medium for the coloring matter so that there is no need for a volatile solvent or other dispersing medium.

According to the embodiment of the invention whereby squeeze-out type transfer elements are produced, the polymerizable composition contains a liquid oil which is miscible with the liquid monomer but is incompatible with the polymer formed by polymerization of the monomer so that the oil separates therefrom as oily droplets trapped within the resinous structure formed. Dye and/or pigments are also dispersed in the polymerizable composition so that the final oily droplets comprise a liquid ink which is pressure-exudable from the resinous binder material to a succession of copy sheets.

According to the second embodiment, in which frangible transfer elements are produced, the polymerizable composition contains a high amount of waxy particles, filler and/or solid pigments or dyestuffs which are insoluble in and incompatible with the composition and disrupt the continuity of the final polymerized layer so that it is relatively brittle and frangible or pressure-transferable in mass. The colorant is preferably a solid undissolved hectograph dyestuff, whereby the transfer layer is used to image a master sheet, or magnetic iron oxide pigment, whereby the transfer layer is used to image record cards or record sheets with magnetizable composition adapted for automatic magnetic sensing. Oils compatible with or soluble in the polymer formed by polymerization may also be included.

The frangibility of the transfer sheets produced according to this second embodiment may be improved, where necessary, by the use of a release layer on the foundation, or by the application of a tacky supercoating over the transfer layer, or by the use of a special receptor coating on the surface of the copy sheet. Such receptive coatings are well known in the art and generally comprise microcrystalline wax, synthetic resin such as polyisobutylene resin and/or filler such as calcium carbonate, clay, or the like.

According to the preferred embodiment, the composition includes a low molecular weight synthetic thermoplastic liquid polymer such as a dimer, trimer, or telomer which preferably is also acrylic, and is compatible or miscible with the liquid monomer and is polymerizable to a solid condition during polymerization of said monomer. Preferred materials of this type are low polymers commercially available under the Registered Trademark Sartomer such as Sartomer SR 350 which is tripropyl trimethoxy acrylate.

Conventional polymerization catalysts are included in conventional amounts in order to hasten polymerization and insure completeness of reaction and uniformity of end result. Peroxide catalysts are preferred such as lauroyl peroxide, benzoyl peroxide, t-butyl peroxide, and the like. Preferably the peroxide catalyst is first uniformly mixed with a vinyl monomer which polymerizes more slowly than the present acrylic esters, such as styrene. In this way the catalyst can be uniformly dispersed throughout the composition in the styrene, and as the sytrene polymerizes and/or copolymerizes, the catalyst will be liberated to uniformly catalyze the polymerization of the more reactive acrylic monomer. This is particularly preferred when the coating composition is applied under atmospheric conditions and subsequently introduced into an inert heated atmosphere for polymerization.

The composition also includes an oleaginous material which may be an oil, a semi-solid oily or waxy material or a solid wax. In cases where the transfer element being prepared is of the squeeze-out type, the oleaginous material is incompatible with the formed resin binder and comprises an oil such as mineral oil, refined rapeseed oil, or the like and may also include a semi-solid material such as lanolin, hydrogenated vegetable oil, lecithin, or the like. In cases where the transfer element being prepared is of the frangible, stencilling type, the oleaginous material may be an oil, semi-solid or solid wax. If an oil, mixture of oils or a semi-solid material is used, it should have a substantial degree of compatibility with the formed resin binder so as to soften the binder to some extent and produce a pressure-transferable layer. This effect is also assisted by the incorporation of relatively large amounts of filler such as clay, bentonite, silica, or the like.

The coloring matter may be varied depending upon the type of product being produced. Squeeze-out carbons and ribbons generally contain pigments such as toned carbon black, alkali blue pigment, magnetic iron oxide, or the like. Pencil carbons of the squeeze-out type generally contain an amount of dyestuff dissolved in the oil vehicle. Frangible carbons and ribbons generally contain solid pigments and dyestuffs such as carbon black, magnetic iron oxide or crystal violet.

The coating compositions are prepared by uniformly mixing the ingredients. Generally the oleaginous material and colorant are mixed to form an ink paste which is thereafter mixed with the polymerizable components immediately prior to the coating step. The composition is applied to a support such as a casting surface or to a flexible foundation, which may take place under atmospheric conditions, as a uniformly thin layer having the desired thickness which generally ranges from about 0.3 to 3 mils (0.0003 to 0.003 inch). The coating is then subjected to an inert atmosphere, such as of nitrogen, carbon dioxide or helium, and is heated to a temperature of from about 180° F to 250° F and preferably from about 200° F to 225° F to polymerize the monomer and/or monomers and other polymerizable materials, if present, and form a solidified pressure-sensitive transfer element on cooling.

FIG. 1 of the drawings illustrates an apparatus which may be used. The web **10** of flexible foundation material such as paper or plastic film is expended from roll **11** and its underside is brought into contact with application roller **12** which applies a continuous thin layer of coating composition **13** to the web from vat **14**. Doctor blade **15** levels the coating to the desired thickness and the coated web travels through heating chamber **16** which is continuously provided with an atmosphere of inert gas such as nitrogen. The heating chamber contains a bank of infrared lamps **17** which heat the polymerizable coating for the required period of time to form the solidified pressure-sensitive layer **18**. Finally the web is collected on take-up roll **19** for further processing such as cutting into ribbons or sheets.

FIG. **2** illustrates the final transfer element having flexible foundation sheet **10** and pressure-sensitive transfer layer **18**.

The following examples are given by way of illustration and should not be considered limitative:

EXAMPLE 1

Ingredients	Parts by Weight
Styrene monomer	3 g.
Lauroyl peroxide	0.4 g.
Hydroxyethyl methacrylate	4 g.
Sartomer SR 350	2 g.
Carbon black	2 g.
Mineral oil	2.4 g.
Hydrated silica	0.1 g.

The lauroyl peroxide is uniformly mixed with the styrene, and the mineral oil and carbon black are uniformly mixed to form an ink paste. The ink paste, styrene and remaining ingredients are uniformly mixed and applied to a flexible paper foundation as a layer having a thickness of about 0.8 mil and heated to a temperature of 250° F in an atmosphere of nitrogen for a period of 30 seconds. The original wet, tacky layer cures to a dry, solidified layer which exudes the ink paste under the effects of imaging pressure while the polymerized resin binder remains bonded on the paper foundation.

EXAMPLE 2

Ingredients	Parts by Weight
Methyl methacrylate	6.
Sartomer SR 350	2.6
Styrene monomer	4.
Lauroyl peroxide	0.6
Castor oil	12.
Refined rapeseed oil	36.
Carbon black	12.
Clay	48.

The above composition is formulated in the same manner as in Example 1 and was coated as a thin layer having a thickness of about 0.5 mil onto a film foundation of polyethylene terephthalate polyester having a thickness of 0.5 mil. The coated film was heated to a temperature of 225° F in a closed atmosphere of nitrogen for a period of about 40 seconds to polymerize the resinous binder material and solidify the coating. The castor oil is compatible to some extent with the binder material and is also miscible with the rapeseed oil. The solidified layer is substantially completely pressure-transferable from the film foundation under the effects of imaging pressure.

It should be understood that the present solvent-free resin systems are suitable for the production of pressure-sensitive transfer elements of all types which heretofore have been produced through the use of preformed resins dissolved in volatile solvents. The present compositions may be cast on a smooth inert casting surface as a temporary support and stripped therefrom after curing to produce self-supporting transfer elements.

We claim:

1. Process for producing pressure-sensitive transfer elements which comprises the steps of:

a. preparing a coating composition by uniformly mixing a resin-binder-forming material consisting essentially of at least 30 percent by weight of a liquid polymerizable acrylic ester monomer selected from the group consisting of aliphatic esters of acrylic and methacrylic acid in which the aliphatic radical is substituted or unsubstituted and contains from one to five carbon atoms, and at least about 10 percent by weight of a low molecular weight synthetic thermoplastic liquid polymer capable of further polymerization to a solid condition, with a quantity of oleaginous material, coloring matter, and a polymerization catalyst for said monomer;

b. applying said composition to a support in the form of a thin coating; and

c. heating said coating in an inert atmosphere to from 180° F to 250° F to effect solidification of said coating by means of polymerization of said monomer and of said liquid polymer to form a solid resinous binder material for said oleaginous material and coloring matter.

2. Process according to claim **1** in which said liquid polymer comprises tripropyl trimethoxy acrylate.

3. Process according to claim **1** in which said oleaginous material comprises a liquid oil which is substantially incompatible with the formed solid resinous binder material and is exudable from said solidified coating together with said coloring matter as an ink under the effects of imaging pressure.

4. Process according to claim **1** in which said oleaginous material is substantially compatible with the formed solid resinous binder material, a filler is present, and the solidified coating is transferable under the effects of imaging pressure.

5. Process according to claim **1** in which the acrylic ester monomer is hydroxyethyl methacrylate.

6. Process according to claim **1** in which the polymerization catalyst is present as a uniform mixture with a vinyl monomer which polymerizes more slowly than said acrylic ester monomer.

7. Process according to claim **1** in which the inert atmosphere is nitrogen.

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