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HEAT-SENSITIVE COPYING SHEET AND METHOD OF MAKING

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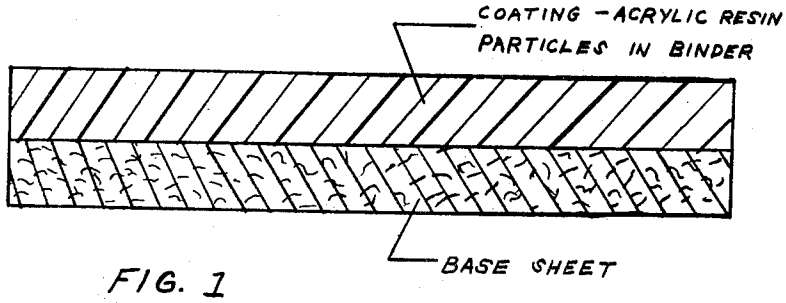


FIG. 1

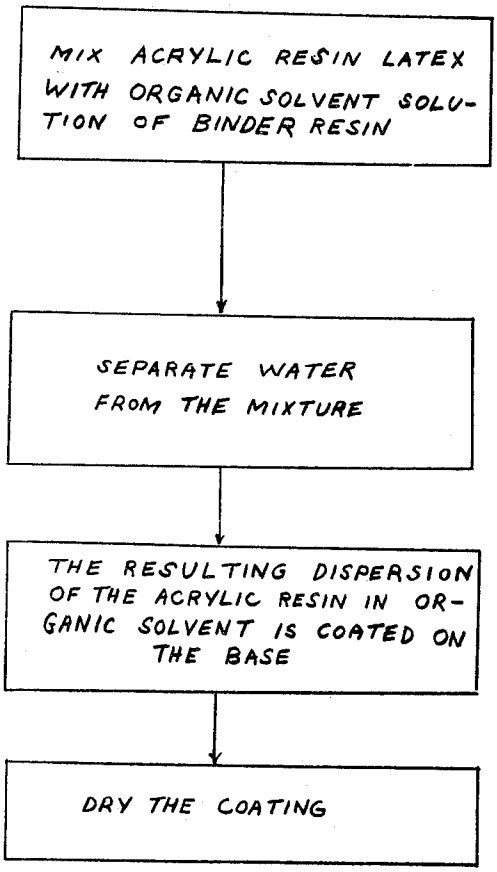


FIG. 2

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HEAT-SENSITIVE COPYING SHEET AND METHOD OF MAKING

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This invention relates to heat-sensitive copying paper useful in preparing copies of printed matter or other graphic originals.

Heat-sensitive copying papers which operate by means of a physical change that is produced by heat are old in the art. U.S. Patent No. 2,710,263 and Reissue Patent No. 24,554 describe heat-sensitive coatings for making copying paper in which the image appearing on the copy sheet results from a physical change in the coating corresponding to the image copied. According to the teachings of these prior art patents a heat-sensitive copying paper can be prepared by coating a dark colored supporting base with a composition consisting of particles of a normally transparent stable organic fusible solid, melting within the range of 60–115° C., dispersed in a solution of a transparent film-forming binder in a volatile solvent, evaporating the solvent without fusing or dissolving the particles so as to provide a non-transparent, infrared transmitting, heat-sensitive layer. A protective layer of film-forming material can be applied over the heat-sensitive layer if desired. Heating the sheet at temperatures corresponding to the melting point of the fusible solid melts the heat-sensitive coating and allows the dark colored base sheet to show through at the heated areas. In making copies of graphic originals, the heated areas would correspond to the image on the original and would result from heat generated by exposing the original to high intensity infrared radiation. Preferably the copy is made by placing the copy sheet on the original with its uncoated side next to the original and then exposing the original through the heat-sensitive copy sheet. In an alternate technique, the original would be exposed to infrared radiation directly with the coated side of the heat-sensitive paper immediately back of it. By this "back-printing" technique it is not necessary, of course, that the heat-sensitive paper be infrared transparent. Both the "back-printing" and the "front-printing" techniques are described in the prior art patents mentioned above and also in U.S. Patent No. 2,859,351.

A problem which has hampered the use of heat-sensitive coatings of the type described in the aforementioned patents is that the pressure-sensitivity of such coatings is greater than is desirable. That is the coatings on copy are easily bruised and marred during handling allowing the dark colored base sheet to show through.

It has been found that heat-sensitive coatings having decreased pressure-sensitivity may be produced by using particles of acrylic resins made by emulsion polymerization as "fusible" particles dispersed in a transparent film of binder. In addition to decreased pressure-sensitivity, because of the finely divided state of the particles (less than 1 micron in diameter), the coating has a high degree of homogeneity as well as maximum covering power for a given weight of resin thereby providing a maximum opacity for said weight of resin.

It has been found that the novel coatings of this invention may be produced by forming a latex of emulsion

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polymerizable vinyl-type resins particularly acrylic resins and then transferring the entire dispersed phase of said latex from its aqueous dispersion medium to a dispersion medium comprising a solution of a transparent film-forming organic binder dissolved in an organic solvent in which solvent said dispersed phase is insoluble. This transfer has been found to be readily accomplished by mixing the latex and said organic solution under considerable agitation, e.g., mechanical stirring. After such mixing, the mixture is permitted to settle into two phases, a water phase and an organic phase. The resin particles are no longer dispersed in the water phase but are now dispersed in the organic phase.

Without being bound on the theory, it is believed that the acrylic resin particles in general are preferentially wetted by organic solvents than by water. Thus, if by sufficient agitation, the emulsified particles can be broken away from the continuous phase (water) and into contact with the organic solution, these particles will be preferentially wetted by said organic solution.

The dispersion of resin particles in the organic solution is then coated on a supporting base of the type described in Reissue Patent No. 24,554, and dried to form the heat-sensitive coating.

While it has been found that temperatures as high as 180° C. may be used in conventional processes and apparatus for making heat-sensitive copies as described in the aforementioned patents, it is preferable that the acrylic resin particles have softening temperatures below 120° C. and advantageously in the range of from about 70° C. to 120° C.

The term "softening temperature" as used in this application should here be defined. Unlike the fusible non-polymeric compositions disclosed in Reissue Patent 24,554, which have clear cut melting points at which there is a transition from the solid to the liquid state, the resinous particles of this invention, being amphorous, have no melting point. The acrylic resins used have narrow temperature regions in which each changes from a viscous or rubbery condition at a temperature above this region to a hard and relatively brittle condition. This transformation is equivalent to the solidification of a liquid to glass; it is not a phase transition. This temperature region is referred to as the "softening temperature." It may also be called the "glass temperature" or "the second order transition temperature."

In this application all proportions are by weight unless otherwise stated.

The latex used is preferably an acrylic resin latex including resins made from the alkyl esters of acrylic and methacrylic acids in which the alkyl groups contain from one to eight carbons such as methyl methacrylate, ethyl acrylate, methyl acrylate, butyl acrylate and ethylhexyl acrylate as well as acrylonitrile and methacrylonitrile. The resin may be a homopolymer of a given acrylic monomer or a plurality of acrylic monomers which may be copolymerized to provide a "tailor-made" resin latex. By the term "tailor-made" is meant that in cases where homopolymers of a given acrylic monomer do not possess a desirable softening temperature, said acrylic monomer may be copolymerized with one or more acrylic monomers to produce an acrylic resin having the desired softening temperature. For example, polyacrylonitrile has a softening temperature well above 120° C. In order to produce an acrylic resin having a desirable softening temperature,

acrylonitrile monomer may be copolymerized with ethyl acrylate monomer having a softening temperature of about 10° C. The acrylic monomers may also be copolymerized with monomers such as acrylamides including acrylamide and methacrylamide, hydroxy compounds such as ethylene glycolmonoacrylate or monoethylacrylate, as well as other olefinically unsaturated monomers as vinyl esters including vinyl acetate and vinyl propionate vinylidene chloride, styrene, alpha methyl styrene, and vinyl toluene.

The primary requirement for the organic solvent used is that it must be one in which the acrylic resin is insoluble. The nature of the solvents in which a given acrylic resin is insoluble is known to those skilled in the art.

While alkyd resins particularly phthalic alkyd resins such as oil modified alkyds have been found to provide desirable film-forming binder material, other conventional organic film-forming binders may be used. The primary requirement is that such binders must be soluble in the organic solvent dispersion medium.

Other operable binders which may be used (conditionally of course upon their solubility in the organic solvent) are, for example, cellulosic polymers such as nitrocellulose and ethyl cellulose, phenolformaldehyde resins and epoxy resins.

In the organic dispersion, it is preferable to use from 1 to 3 parts by weight of acrylic resin for each part of binder. The proportions of the solvent will vary with the nature of the acrylic resin and the binder. Preferably from 2 to 4 parts by weight of solvent are employed for each part of binder.

In the drawings:

FIG. 1 is a diagram of the copying sheet.

FIG. 2 is a flow sheet of the method.

This invention is illustrated by the examples which follow:

Example 1

A mixture of 75 parts of acrylonitrile monomer, 50 parts of ethyl acrylate monomer, 0.5 part of ammonium persulfate, 750 parts of water and 50 parts of emulsifying agent (14% octylphenoxy polyethoxyethanol and 86% Triton X200, the sodium salt of an alkyl aryl sulfonate) are heated to reflux at 74° C. and maintained at said temperature for 45 minutes during which time 375 parts of a mixture comprising 60% acrylonitrile and 40% ethyl acrylate monomer are gradually added. After the addition is completed, reflux is continued for 2 hours during which time the temperature gradually rises to 94° C. The resulting acrylic latex has a solids content of 38.3% by weight.

210 parts of the resulting acrylic latex are then mixed on a high speed stirrer for 30 minutes with a solution of 32 parts of a medium oil modified non-oxidizing type alkyd comprising 43% phthalic anhydride, 33% coconut oil and 24% glycerol (acid No. 6–10) and 105 parts of xylol. The resulting mixture is then poured into an excess of water (240 parts) while stirring. This mixture is allowed to stand until it separates into a water and oil phase. The water phase is then removed. Then 74 parts of xylol are added to the remaining oil phase (307 parts) and a water-xylol mixture (135 parts) is removed by distillation. This procedure is repeated, 60 parts of xylol being added and 107 parts of water-xylol mixture being distilled off. 107 parts of xylol are then added to the resulting mixture which is a dispersion of the acrylic resin in the xylol-alkyd solution (total solids content by weight of the mixture is 25.7%). The resulting dispersion is applied to 8# Black Fenmore paper (Schweitzer Paper Company) as a thin film of 2 to 2.5 mg. per square inch and the resulting coated sheet is air dried.

Example 2

A mixture of 250 parts of methyl methacrylate, 60 parts of lauryl sodium sulfate emulsifying agent, 0.5 part of ammonium persulfate and 750 parts of water are heated to reflux at 81° C. and maintained at said temperature for one hour while 250 additional parts of methylmethacrylate are gradually added. The resulting methylmethacrylate resin latex has a solids content of 39.7% by weight.

210 parts of the resulting acrylic latex are then mixed on a high speed stirrer for 30 minutes with a solution of 26 parts of an oxidizing type medium oil alkyd comprising a phthalic anhydride-glycerol alkyl containing 50% soya oil in a solvent comprising 26 parts of mineral spirits and 85 parts of a hydrocarbon solvent, predominantly aliphatic in nature having a boiling range of 157.2° to 201.1° C., a K.B. value of 44.5 and an aniline point of 110. A small amount of magnesium sulfate (less than 0.5%) is added and the mixture is stirred for another 5 minutes. The resulting mixture is then poured into 400 parts of water and permitted to stand until there is a separation into an oil and water phase. The water phase is separated and the remaining dispersion of polymethylmethacrylate resin in the organic solution is applied to a black paper in accordance with the procedure set forth in Example 1.

It has been found that the stability of the dispersion of the acrylic resin in the organic solution is increased and that the resulting coated sheet is improved if the water is not completely separated from the organic dispersion. It is desirable to have residual amounts of water not exceeding 4% of the total organic dispersion weight.

While there have been described what are considered to be the preferred embodiments of this invention, it will be understood that the practice of this invention is not limited to the resins described in the specific examples but that various modifications may be made therein without departing from the scope of the invention as it is defined in the appended claims.

What is claimed is:

1. The method of making a heat-sensitive copying sheet adapted on being placed in contact with a graphic original and on irradiation of said graphic original with high intensity infrared radiation to provide an image on said copying sheet corresponding to the graphic original which method comprises mixing a latex comprising acrylic resin particles having a softening temperature within the range of 70° to 120° C. dispersed in water with a solution comprising a transparent film-forming organic binder infusible within said softening range dissolved in an organic solvent, said particles being insoluble in said solution, separating the water from the resulting mixture to produce an organic dispersion of said acrylic resin particles in said solution, coating said resulting dispersion on a non-metallic supporting base and drying said coating.

2. The method claimed in claim 1 wherein a minor amount of water is not separated, said water constituting less than 4% of the total weight of said organic dispersion.

3. The method claimed in claim 1 wherein said acrylic resin comprises an acrylic ester.

4. The method claimed in claim 1 wherein said acrylic resin is methyl methacrylate.

5. The method claimed in claim 1 wherein said acrylic resin comprises a copolymer of acrylonitrile and ethyl acrylate.

6. A heat-sensitive copying sheet comprising a non-metallic supporting base and a visibly opaque heat-sensitive coating thereon, said coating being made by mixing a latex comprising acrylic resin particles having a maximum diameter of 1 micron and a softening temperature within the range of 70° to 120° C. dispersed in water with a solution comprising a transparent film-forming organic binder infusible within said softening temperature range dissolved in an organic solvent, said particles being insoluble in said solution, separating the water from the resulting mixture to produce an organic dispersion of

said acrylic resin particles in said solution, coating said resulting dispersion on said supporting base and drying said coating.

7. The copying sheet of claim 6 wherein a minor amount of water, less than 4% by weight of the total organic dispersion is not separated with the rest of the water.

8. The copying sheet of claim 6 wherein said acrylic resin comprises an acrylic ester.

9. The copying sheet of claim 6 wherein said acrylic resin is methyl methacrylate.

10. The copying sheet of claim 6 wherein said acrylic resin comprises a copolymer of acrylonitrile and ethyl acrylate.

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