

# United States Patent

Blose et al.

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[54] **THERMAL TRANSFER MEDIUM FOR PRODUCING SCRATCH AND SMUDGE RESISTANT MARKS**

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117/155 L, 260/15, 260/39 P

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

[56]

## References Cited

### UNITED STATES PATENTS

|           |        |                           |          |
|-----------|--------|---------------------------|----------|
| 3,382,088 | 5/1968 | Noda .....                | 117/36.1 |
| 3,467,539 | 9/1969 | Schlotzhauer et al. ..... | 117/36.1 |
| 3,519,464 | 7/1970 | Balster et al. .....      | 117/36.1 |

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[57]

## ABSTRACT

A thermal transfer medium comprising a base having a transferable coating composition thereon. The coating composition comprises about 3 to 40 percent by weight of a cellulosic polymer; about 15 to 70 percent by weight of a thermoplastic aminotriazine-sulfonamidealdehyde resin; about 3 to 40 percent by weight of a plasticizer; and about 1 to 45 percent by weight of a sensible material.

15 Claims, No Drawings

# THERMAL TRANSFER MEDIUM FOR PRODUCING SCRATCH AND SMUDGE RESISTANT MARKS

## BACKGROUND OF THE INVENTION

This invention relates to thermal transfer media and to a process for making the same. More particularly, this invention relates to thermal transfer media, having transferable coating compositions thereon, which are suitable for applications requiring transfer of the coating composition from the transfer medium to a recording medium. Transfer pressure is applied by means of pressure and heat such as the impact of heated type or pressure from other heated marking instruments in selected areas, either to the back of a transfer medium which has a transferable coating composition thereon or to the back of a recording medium to cause break-away of the coating composition from the transfer medium and adherence of such broken-away coating composition to the recording medium.

Transfer media such as carbon paper and typewriter ribbons have, of course, been known and used for many years. Lately, however, the placing of various types of thermally printed marks on recording media to be handled and sensed by data processing equipment has become a matter of increasing interest and special thermal transfer sheets and printed ribbons have been developed to meet the requirements of such data processing equipment.

One of the greatest problems encountered with marks thermally printed on recording media is the great tendency for the printed marks to scratch or smudge. The marks thermally printed on the recording medium usually become scratched or smudged when the printed medium is passed through ordinary commercial transactions and when the printed medium is passed through data processing equipment. This problem of scratching and smudging is encountered even with some of the most recently developed transfer media. When this scratching or smudging occurs, the reliability with which the true mark can be automatically sensed is severely impaired even though the impairment may sometimes be comparatively slight by visual standards.

The present invention provides a thermal transfer medium which is capable of producing suitable thermally printed marks on a recording medium which have sufficient resistance to scratching and smudging when the printed medium is passed through ordinary commercial transactions and when the printed medium is processed through data processing equipment so that the printed marks do not sustain any change sufficient to affect the accuracy of the sensing operation.

The present invention provides thermal transfer media, having colored transferable coating compositions thereon, which may be used in the printing of colored code bars on recording media such as paperboard marking tags used by merchandising institutions to identify inventory. Such color-coded tags have resulted in a major breakthrough in machine readable media technology. In a typical system, white paperboard tags are printed with font which is readable by humans and are encoded or printed with different colored bars by a color-coded tag printer which are readable by an optical scanning device known as a color-coded tag reader. The colored printed bars may be separated thereby allowing the white background of the paper to form a third colored bar. The tag itself offers many business system advantages which include attachment methods, base stock variety, information capacity and flexibility. The color-coded tag serves as a medium to transfer data between the color-coded tag printer, which encodes data contained in a source document onto the tag, and the color-coded tag reader which enters the color-coded data into the business system usually at the point of sale. The color-coded tag reader utilizes optical scanning to sense and distinguish the different colored bars which have been encoded on the tag by the tag printer in a binary pattern and to convey the encoded information contained in the bars to the business system.

In a color-coded tag system as described above, it is very important that the different colored bars which are encoded on the tag have a high resistance to scratching and smudging so

that the information contained in the bars can be correctly read by the optical scanning device of the color-coded tag reader.

The present invention also provides thermal transfer media, having improved transferable coating compositions, which may be used in the encoding or printing of paper records such as checks, bank deposit slips, credit charge slips and the like with magnetic symbols which can be recognized by electronic accounting equipment or which may be used as one-time carbon ribbons or papers.

It will be readily apparent that the principles of the present invention can be applied whether the thermal transfer medium is designed to deposit marks suitable for sensing visually, by optical means, by photo-electric means, by magnetic means, by electroconductive means, or by any other means sensitive to a special material in the coating.

## PRIOR ART

20 The present invention comprises a transfer medium having a transferable coating composition thereon. The coating composition comprises a cellulosic polymer, an aminotriazine-sulfonamide-formaldehyde resin, a plasticizer and a sensible material.

25 The thermal transfer medium of the present invention produces thermally encoded or printed marks on a recording medium which possess excellent scratch and smudge resistant properties.

30 The most pertinent prior art is found in the following patents which disclose transfer media which produce printed marks on recording media by means of pressure such as the impact of type or pressure from other marking instruments. U.S. Pat. No. 2,984,582 discloses a transfer medium having a porous, thermoplastic resin layer containing a transferable ink. The ink is released by the resin layer onto a recording medium without transfer of the resin layer onto the recording medium. U.S. Pats. Nos. 2,671,734; 2,822,288; 3,337,361 and 3,340,086 disclose transfer media which produce encoded or

35 40 printed marks on a recording medium. None of these patents disclose the thermal transfer medium having the transferable coating composition of the present invention. U.S. Pat. No. 3,062,676 discloses a transfer medium having a coating composition which is formed of a plurality of coatings. The coatings are transferred to a recording medium thereby

45 50 producing encoded or printed marks on the medium which possess good smudge resistant properties. U.S. Pat. No. 3,087,832 discloses a transfer medium having a coating composition which comprises a magnetic pigment mixed in a silicone resin and a silicone rubber binder system. The coating composition has a top coating of wax which aids in the adherence of the magnetic transfer coating to a recording medium upon transfer thereto. U.S. Pat. No. 3,375,125 discloses a

55 60 transfer medium having a coating composition which comprises ethyl cellulose, a resin binder, mineral oil, a wax and a pigment. The coating composition is transferred to a recording medium thereby producing encoded or printed marks on the recording medium which possess good smudge resistant properties.

65 70 75 The prior art does not disclose the novel thermal transfer medium of the present invention which produces thermally encoded or printed marks on a recording medium possessing excellent scratch and smudge resistant properties.

## SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a thermal transfer medium comprising a base having a transferable coating composition thereon, said coating composition comprising about 3 to 40, preferably about 15 to 25, percent by weight of a cellulosic polymer; about 15 to 70, preferably about 50 to 65, percent by weight of a thermoplastic aminotriazine-sulfonamide-aldehyde resin; about 3 to 40, preferably about 15 to 25, percent by weight of a plasticizer; and about 1 to 45, preferably about 2 to 20, percent by weight

of a sensible material. The above percents by weight are based on the total weight of the transferable coating composition.

In further accordance with the present invention, the thermal transfer medium of the present invention is produced by a process which comprises applying the above named components of the coating composition to a suitable base by means of a volatile organic solvent carrier. The solvated coating composition is spread uniformly over the base and the volatile organic solvent carrier is then allowed to evaporate thereby leaving a transferable coating composition deposited on the base.

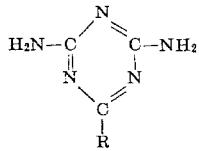
#### DETAILED DESCRIPTION OF THE INVENTION

The cellulosic polymer can be any of the well known polymers such as cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose methyl ether, cellulose ethyl ether, cellulose nitrate and the like and mixtures thereof.

The thermoplastic aminotriazine-sulfonamide-aldehyde resin used in the present invention is a co-condensation product of a cyclic aminotriazine, an aromatic monosulfonamide and an aldehyde such as formaldehyde. The thermoplastic resin should preferably be completely condensed.

The thermoplastic aminotriazine-sulfonamide-aldehyde resin may be prepared from an aromatic monosulfonamide having two reactive amide hydrogens, a cyclic aminotriazine having at least two primary amino groups and an aldehyde such as formaldehyde or paraformaldehyde. If desired, either or both of the first-mentioned components may be separated reacted with the aldehyde to form a thermoplastic sulfonamide-aldehyde resin or a B-stage partially condensed aminotriazine-aldehyde resin, respectively, before being co-condensed. The aromatic sulfonamide may comprise toluene sulfonamide, for example, ortho- or para-toluene sulfonamide or mixtures thereof, benzene sulfonamides, or the alkyl derivatives of such sulfonamides, and the like, in which the sulfonamido group is attached directly to the aromatic nucleus through the sulfur atom.

The cyclic aminotriazine compound may comprise a compound having at least two amino groups as represented by the following formula:



wherein R is hydrogen, alkyl containing 1 to about 8 carbon atoms, aryl, aralkyl, amino, and the like.

The following are typical aminotriazine compounds within the above formula:

- 2,4-diamino-1,3,5-triazine
- 2-methyl-4,6-diamino-1,3,5-triazine
- 2(3-hydroxy butyl)-4,6-diamino-1,3,5-triazine
- 2-heptyl-4,6-diamino-1,3,5-triazine
- 2-phenyl-4,6-diamino-1,3,5-triazine
- 2-benzyl-4,6-diamino-1,3,5-triazine
- 2,4,6-triamino-1,3,5-triazine (melamine)

In place of melamine as the aminotriazine compound, one can use methyl melamine or other alkyl derivatives of melamine, that is, n-alkyl melamines, such as the mono- or dialkyl derivatives where the alkyl group may be methyl, ethyl, propyl, butyl, and the like, up to about 8 carbon atoms.

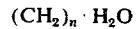
Also, the B-stage methylol aminotriazine resin can be modified by forming the alkyl ether of the methylol aminotriazine. For example, this can be done by taking an A-stage methylol aminotriazine, that is, the tri-, tetra- or pentamethylol aminotriazine, and then converting to the B-stage resin in the presence of an alkanol such as methanol, ethanol,

propanol, butanol, and similar alkanols containing up to about eight carbon atoms. When using methanol, the resin would be the mono- or dimethyl ether of tri-, tetra- or pentamethylol aminotriazine, in partially condensed form. Also, alkanol derivatives of the aminotriazine in which the alkyl group contains more than about three carbon atoms may be formed during the course of the co-condensation reaction by introducing the aminotriazine in a solution of an alcohol such as butanol. It will be noted that the aminotriazine reacts as an amide rather than as an amine.

The relative quantities of the materials to be co-condensed are critical only to the extent that sufficient aldehyde should be used to produce a completely condensed product; if too large a quantity of the aminotriazine is used, the final product will be a thermosetting product, which is not desired; and if too small a quantity of the aminotriazine is used, the softening point of the product will differ only slightly from the softening point of the sulfonamide-formaldehyde resin and may not have insolubility in the desired solvents. Also, the amount of the sulfonamide is dependent upon the number of primary amino groups in the aminotriazine. For example, it is preferred to use about three times (on a molar basis) as much of the sulfonamide as the aminotriazine when the aminotriazine contains two amino groups, and about five times (on a molar basis) as much sulfonamide when the aminotriazine contains three amino groups. In other words, the aminotriazine or B-stage aldehyde-aminotriazine resin is preferably from about 20 to 33 mol percent of the amount of the monosulfonamide or the aldehyde-monosulfonamide resin, although the former may be as great as about 5 mol percent and as little as about 17 mol percent of the latter.

Generally, when preparing the alkanol modified resin, it is necessary to use additional quantities of formaldehyde over and above that required for the alkanol modification so as to provide for subsequent co-condensation with the sulfonamide-formaldehyde resin. The B-stage aminotriazine-formaldehyde resin, that is, the methylol aminotriazine, must have at least two methylol groups and preferably three such groups in order to successfully carry out the subsequent co-condensation with the sulfonamide resin.

The thermoplastic resin may be prepared using as reactants either formaldehyde or its polymer, paraformaldehyde, which polymer has the general formula



where n is 6 or greater. This monomer and its polymer should be distinguished from polyaldehydes such as glyoxal containing a plurality of aldehyde groups in a stable molecule.

Typical modes of preparation of the thermoplastic aminotriazine-sulfonamide-aldehyde resin used in the present invention are found in U.S. Pat. No. 2,938,873 in Examples 1 through 25. These Examples are incorporated herein as a part of this specification.

In a preferred embodiment, the thermoplastic aminotriazine-sulfonamide-aldehyde resin is a co-condensation product of a melamine, an aromatic sulfonamide and an aldehyde such as formaldehyde. The thermoplastic resin should preferably be completely condensed. The thermoplastic melamine-sulfonamide-aldehyde resin may be prepared from an aromatic mono-sulfonamide having two reactive hydrogens, that is, two reactive amide hydrogens, a melamine or a melamine derivative having at least two functional amide groups and formaldehyde or paraformaldehyde. If desired, either or both of the first-mentioned components may be separately reacted with formaldehyde to form a thermoplastic sulfonamide-aldehyde resin or a B-stage partially condensed melamine-aldehyde resin, respectively, before being co-condensed. The aromatic sulfonamide may comprise a mixture of ortho- and para-toluene sulfonamides, benzene sulfonamide or the alkyl derivative thereof or a toluene sulfonamide wherein the sulfonamido group is attached directly to the aromatic nucleus through the sulfur atom.

The B-stage partially condensed melamine-aldehyde resin (methylol melamine resin) is the water soluble, thermofusible reaction product of melamine and formaldehyde or paraformaldehyde. In place of melamine, one can use the methyl melamine or other alkyl derivatives of melamine such as the mono- or dialkyl derivatives where the alkyl group may be methyl, ethyl, propyl, butyl or the like.

Also, the B-stage melamine-aldehyde resin can be modified by forming the alkyl ether of the melamine-aldehyde resin. This can be done by taking an A-stage melamine-aldehyde resin, that is, the tri-, tetra- or pentamethylol melamine resin, and then converting it to the B-stage resin in the presence of an alkanol such as methanol, ethanol, propanol, butanol or the like. When using methanol, the modified B-stage resin would be the mono-, di- or trimethyl ether of tri-, tetra- or pentamethylol melamine in partially condensed form.

The relative quantities of the materials to be co-condensed are critical only to the extent that more than about 20 percent by weight of the unmodified melamine-aldehyde B-stage resin in the final product will produce a thermosetting product, which is not desired, and, if too small a quantity of the melamine resin is used, the softening point of the product will differ only slightly from the softening point of the aromatic sulfonamide-aldehyde resin. In other words, the amount by weight of the sulfonamide-aldehyde resin should be at least four times the amount of the unmodified B-stage melamine-aldehyde resin. When the unmodified melamine-aldehyde B-stage resin is employed, it is preferred to use about 16 percent thereof based on the weight of the final co-condensed resin, that is, about five times as much of the sulfonamide-aldehyde resin as the unmodified B-stage melamine-aldehyde resin. When the melamine derivatives or the modified B-stage melamine resins are used, greater relative quantities can be employed up to about 25 to 35 percent by weight of the final product, that is, up to about 50 percent by weight of the sulfonamide-aldehyde resin. Generally, when employing a melamine derivative to form the B-stage partially condensed resin or when preparing the alkanol modified melamine resin, it is desirable to use greater quantities of the aldehyde so as to provide additional methylol groups for subsequent co-condensation with the sulfonamide-aldehyde resin. The B-stage melamine-aldehyde resin, that is, the methylol melamine resin, must have at least two methylol groups and preferably three or four such groups in order to successfully carry out the subsequent co-condensation with the sulfonamide resin.

The various melamine derivatives having at least two functional amide groups, which are useful substitutes for melamine for the purposes of the present invention, include all of such derivatives mentioned in the foregoing discussion. Stated most simply, by way of summary, they include alkyl melamines having preferably no more than one alkyl substituted amido nitrogen and monohydric alkanol modified methylol and alkyl methylol melamines.

The melamine-sulfonamide-aldehyde resin can be prepared using either formaldehyde or its polymer, paraformaldehyde, as reactants. This monomer and its polymer, wherein the same atoms are present in the same proportion, should be distinguished from isomerides of formaldehyde such as diformaldehyde which contains a plurality of aldehyde groups in a stable molecule.

Typical modes of preparation of the thermoplastic melamine-sulfonamide-aldehyde resin used in the present invention are found in U.S. Pat. No. 2,809,954, in Examples 1 through 15. These Examples are incorporated herein as a part of this specification.

The aminotriazine-sulfonamide-aldehyde resin has a higher softening point than the well-known sulfonamide-aldehyde resins and has some characteristics which are in no way similar to the completely condensed aminotriazine-aldehyde resins and other characteristics which are in no way similar to the thermoplastic sulfonamide-aldehyde resins. The aminotriazine-sulfonamide-aldehyde resin not only has a higher melting point than the sulfonamide-aldehyde resins,

but it will release solvents more rapidly than such resins and does not exhibit cold flow at room temperature as do the sulfonamide-aldehyde resins. On the other hand, the aminotriazine-sulfonamide-aldehyde resin, unlike the aminotriazine-aldehyde resin, is soluble in certain solvents and is thermoplastic. The overall character of the aminotriazine-sulfonamide-aldehyde resin makes it especially suitable for the manufacture of pigments. For example, the aminotriazine-sulfonamide-aldehyde resin can be highly colored and, even though thermoplastic, can be readily ground to a finely divided condition at temperatures below about 100° C. Most thermoplastic resins will either soften at the temperature encountered during grinding or will tend to ball up or agglomerate, even at temperatures below the softening point, probably due to cold flow under the pressure of the grinding elements. The aminotriazine-sulfonamide-aldehyde resin is brittle and friable below its softening point and is not hornlike and tough as are most thermoplastic resins. The aminotriazine-sulfonamide-aldehyde resin is insoluble in many common vehicles and can therefore be suspended in such vehicles without coalescence or agglomeration.

The plasticizer used in the present invention is employed to modify the properties of the thermoplastic polymeric material and the aminotriazine-sulfonamide-aldehyde resin to produce a flexible and non-brittle thermal transfer medium. Suitable plasticizers include adipic acid esters, phthalic acid esters, ricinoleic acid esters, sebacic acid esters, succinic acid esters, chlorinated diphenyls, citrates, epoxides, glycerols, glycols, hydrocarbons, chlorinated hydrocarbons, phosphates, toluenesulfonamides and the like and mixtures thereof. The plasticizer should be compatible with the thermoplastic polymeric material and preferably is a solid at room temperature.

The sensible material used in the present invention can be any material which is capable of being sensed visually, by optical means, by photoelectric means, by magnetic means by electroconductive means or by any other means sensitive to the sensible material. The sensible material can be an inorganic or organic material such as a coloring material, namely, a dye or a pigment, a magnetic material or any other material capable of being sensed and which is compatible with the coating composition.

Suitable sensible materials include phthalocyanine dyes such as Monastral Green B (color index No. 74260), Monastral Green G (color index No. 74260), Sherwood Green (color index No. 42000) and Tropical Brilliant Green (color index No. 42040); fluorescent rhodamine or xanthene dyes such as rhodamine B Extra (color index No. 45170), rhodamine GDN Extra (color index No. 45160), xylene red (color index No. 45100), rhodamine 5G (color index No. 45105), rhodamine G (color index No. 45150), and rhodamine 2B (color index No. 45151); fluorescent naphthalimide dyes such as brilliant yellow 6G (color index No. 29000) which has the formula 4 amino 1,8 naphthal 2',4' dimethyl phenylimide, other fluorescent naphthalimide dyes such as (4n-butyl-amino) 1,8 naphthal n-butyl imide and 4 amino 1,8 naphthal p-phenyl imide; other dyes or pigments such as malachite green (color index No. 42000); cadmium primrose (color index No. 77199), chrome yellow (color index No. 77600), Ultramarine Blue (color index No. 77007), Phthalocyanine Blue (color index No. 74160), Lake Red C (color index No. 15585), Sodium Lithol Red (color index No. 15630), titanium dioxide and zinc oxide; magnetic metal oxides such as iron oxide, cobalt oxide and nickel oxide; finely divided metals and alloys such as bronze, stainless steel, iron, cobalt, nickel and chrome; and miscellaneous coloring materials such as carbon black, conductive carbon and charcoal.

As an example of a sensible material which is not normally visible, but can be detected, a small amount of a material such as 4-methyl-7-diethylamino coumarin will not color a coating composition when it is exposed to ordinary light but will produce a bright blue color when the coating composition is exposed to ultraviolet light.

The sensible material can include any luminescent, fluorescent or phosphorescent material, either organic or inorganic, or any materials which are partially visible or substantially invisible, in normal or ordinary light, and which become visible or emit energy when exposed to light or energy differing in kind or wave length from that emitted by the luminescent material. The term luminescent material is intended to include and denote both fluorescent materials, which are activated by energy of shorter wave length and emit energy of longer wave length, and phosphorescent materials which continue to emit light or energy after excitation is discontinued.

The above-named sensible materials constitute only a fraction of the many different sensible materials that can be used in the present invention and are not to be construed as limiting the scope of the suitable sensible materials that can be used in the present invention. Any of the above-named sensible materials can be used alone or in combination with each other or in combination with other suitable sensible materials not specifically named above. The sensible material need only be suitable for the sensing required, have a high resistance to scratching and smudging when the coating composition is transferred onto the recording medium and be compatible with the coating composition.

The sensible material can be chosen so that the transferred coating composition will reflect a certain amount of light within a particular wave length. For example, a black sensible material can be chosen so that the transferred coating composition has a diffused reflectance of less than 15 percent of light between a wave length of 600 and 1200 nanometers and a green sensible material can be chosen so that the transferred coating composition has a diffused reflectance of less than 15 percent of light between a wave length of 600 and 750 nanometers, 50 percent of light between a wave length of about 820 and 870 nanometers, and greater than 80 percent of light between a wave length of 900 and 1200 nanometers. The wave length of light between 600 and 1200 nanometers is within the visible and the near infra-red spectrum. The choosing of a sensible material for such optical properties is useful in an optical sensing device.

The base to which the transferable coating composition is applied can be a thin material such as a film, web, sheet, ribbon, fabric or the like. The preferred base is a film of polyethylene terephthalate, however, other bases can be used. For example, cellulosic materials, paper, cellophane, nylon, rubber hydrochloride, polyethylene, polypropylene and the like are acceptable bases when used in the form of a film, web, sheet, ribbon, fabric or the like. The base should have a thickness of about 0.2 to 2, preferably of about 0.3 to 0.8, mils. The base should be such that the transferable coating composition adheres to the base in a proper manner prior to transfer of the coating composition to the recording medium and the transferable coating composition is released from the base in a proper manner upon transfer. The base should be limited in thickness to permit a full realization of the capability of the transferable coating composition to deposit marks having sharp, clear edge definition on a recording medium. The base should also possess uniform tensile and other physical properties to insure uniform transfer of the coating composition onto a recording medium.

At times it may be desirable to enhance the transfer of the transferable coating composition from the base to the receiving medium. This can be achieved by using a release coating composition between the transferable coating composition and the base. The release coating composition can be applied to the base prior to the application of the transferable coating composition. A number of release coating compositions can be used. Among these coating compositions are waxes and waxes containing polymeric additives such as polyvinyl alcohol and carboxy methyl cellulose.

The wax used in the present invention can be a wax having a melting point ranging between about 140 to 220, preferably about 155 to 200, °F. as determined by ASTM D-127. Suitable

waxes include natural waxes such as carnauba, montan and the like and mixtures thereof; synthetic waxes such as hydrogenated, amide, chlorinated, alkene or olefinic, miscellaneous and the like and mixtures thereof; and petroleum waxes such as microcrystalline, paraffin and the like and mixtures thereof.

The term wax, as used herein, defines a class of waxes which is characterized by a particular degree of hardness as determined by a needle penetration test ASTM D-1321. The needle penetration test measures the depth to which a weighted needle penetrates a sample of wax. In the needle penetration test, a wax sample is melted by heating it to about 30° F. above its melting point and is then solidified by cooling to 77° F. The hardness of the wax is measured with a penetrometer whereby a standard needle, under a load of 100 grams, is applied to the wax sample for 5 seconds. The depth to which the needle penetrates the wax during the 5 second time interval is measured in tenths of a millimeter. If the needle penetrates the wax to a depth of 0.2 millimeter, the hardness rating of the wax is 2. If the needle penetrates the wax to a depth of 0.8 millimeter, the rating of the wax is 8, and so forth. The waxes which can be used according to this invention are those which have a rating from about 0.5 to 10, preferably about 1 to 9. The wax can be an animal, mineral, petroleum, synthetic or vegetable wax or a mixture thereof so long as the wax is stable, can be meltable, emulsifiable or solvent dispersible, has the required degree of hardness and has the above indicated melting point range. The release coating can be applied to the base by roll coating, knife coating or by a similar means from a hot melt, emulsion or solvent dispersion of the wax.

The transferable coating composition containing the sensible material can be applied to the base in the following manner to produce the transfer medium of the present invention.

The aminotriazine-sulfonamide-aldehyde resin and the sensible material can be added to the volatile organic solvent with constant stirring until a composition having a uniform consistency is obtained. The cellulosic polymer and the plasticizer can then be added to the volatile organic solvent with constant stirring until a composition having a uniform consistency is obtained. About 500 to 100, preferably about 300 to 150, parts of organic solvent is usually used per 100 parts of cellulosic polymer, aminotriazine-sulfonamide-aldehyde resin, plasticizer and sensible material used. However, the ratio of solvent to the aforementioned components is usually not particularly critical. The aminotriazine-sulfonamide-aldehyde resin can be soluble, partially soluble or insoluble in the volatile organic solvent so that the aminotriazine-sulfonamide-aldehyde resin is dissolved or dispersed in the solvated coating composition. The solvated coating composition can then be milled until a uniform composition is obtained. The sensible material can be added separately to the coating composition or the sensible material can be mixed, dispersed or dissolved in the aminotriazine-sulfonamide-aldehyde resin and then added to the coating composition. The sensible material can be added to the aminotriazine-sulfonamide-aldehyde resin during its production or after its production. Specific details for adding the sensible material to the resin are contained in U.S. Pat. No. 2,809,954 in Examples 6 through 15 and in U.S. Pat. No. 2,938,873 in Examples 9 through 25. These Examples are incorporated herein as a part of this specification.

The transferable coating composition can be applied to the base by roll coating, knife coating or by a similar means. The volatile organic solvent can be evaporated at ambient temperature or can be evaporated by the application of gentle heat thereby leaving a transferable coating composition having a thickness of about 0.1 to 0.4, preferably about 0.15 to 0.3, mils deposited on the base.

Suitable volatile organic solvent carriers for the coating composition include aliphatic and aromatic hydrocarbon solvents such as mineral spirits, naphtha, xylene, toluene and mixtures thereof. Other suitable organic solvents include isopropyl alcohol, isobutyl alcohol, 2-heptanol, isoamyl

acetate, ethyl amyl ketone, diisobutyl ketone, carbon tetrachloride, carbon disulfide, methyl alcohol, ethyl alcohol, ethyl acetate, butyl acetate, acetone, methyl isobutyl ketone, methyl cellosolve, butyl cellosolve, methylene chloride, trichlorethylene and the like and mixtures thereof. The thermoplastic polymeric material and the plasticizer should be soluble or at least partially soluble in the volatile organic solvent so that there is a co-mingling of the thermoplastic polymeric material and the plasticizer. One of the above suggested solvents or a mixture thereof can be selected with this criteria in mind.

The above process for producing the transfer medium of the present invention is only illustrative and can be varied within reasonable limits to produce the transfer medium of the present invention.

#### PREFERRED EMBODIMENTS

The following Examples illustrate the present invention and modes of carrying out the invention.

#### EXAMPLE 1

A typical thermoplastic aminotriazine-sulfonamide-aldehyde resin is prepared in the following manner. 360 parts by weight of a mixture of ortho- and para-toluene sulfonamide-formaldehyde resins are melted at a temperature of 60° to 70° C. and are then heated to a temperature of 125° C. At this temperature, 78.4 parts by weight of B-stage unmodified melamine-formaldehyde resin are added and dissolved therein and heating is continued. The reaction mixture becomes clear at a temperature of about 150° C. and heating is continued up to a temperature of 170° C. and held there for about 10 minutes. Upon cooling, the co-condensed resin begins to solidify at a temperature of about 115° C. The completely condensed product is a clear water-white resin which, below a temperature of about 100° C., is brittle, friable and is easily ground in a micropulverizer or by wet ball milling into a finely divided powder having a particle size of about 4 microns. The completely condensed resin has a softening point at a temperature of about 115° C. Thermoplastic aminotriazine-sulfonamide-aldehyde resins having substantially the same physical properties as the above prepared resin are prepared in accordance with Examples 2 through 6 of U.S. Pat. No. 2,809,954 and Examples 2 through 9 of U.S. Pat. No. 2,938,873. These Examples are incorporated herein as a part of this specification.

A sensible material is incorporated in any of the foregoing clear resins having substantially the same physical properties when the reaction mixture reaches a temperature of between 150° and 160° C. while the reaction mixture is heated up to a temperature of between 170° to 180° C. or by melting the finished resin at a temperature between 130° to 160° C. and adding the sensible material to the melt, solidifying and regrinding the resin. Where applicable, the solidified resin and the sensible material may be dissolved in a ketone or an ester solvent, the solvent evaporated and the composition of sensible material and resin then ground to a fine powder. About 1 to 50 parts by weight of the sensible material is added to 100 parts by weight of the resin depending upon the properties desired in the coating composition of the transfer medium.

#### EXAMPLE 2

A green transfer medium, that is, a printing ribbon, was prepared in the following manner using the solvanted coating composition described below:

##### Solvanted Coating Composition

| Component  | Parts By Weight |
|--|-----------------|
| Cellulose Acetate Butyrate-One-Half Second Viscosity Grade (1)   | 4.5             |
| Melamine-Sulfonamide-Formaldehyde Resin Containing a Fluorescent Green Dye and a Phthalocyanine Green Toner—A-18 (2) | 18.4            |

|   |   |
|---|---|
| 5 | 10  |
|   | N-ethyl-p-toluenesulfonamide (3)            |
|   | Monastral Green B phthalocyanine Polychloro |
|   | Copper Toner—Color Index No. 74260 (4)      |
|   | Methyl Ethyl Ketone                         |
|   | Total: 100.0                                |

1. Marketed by Eastman Chemical Products, Inc., Kingsport, Tennessee, U.S.A. under the trade designation of EAB-381. This polymer contains 50 percent by weight combined cellulose residue, 37 percent by weight combined butyryl, 13 percent by weight combined acetyl and 2 percent by weight of free hydroxyl in the cellulose residue. This polymer yields a viscosity determination of one-half second when tested in accordance with ASTM D-817-64 wherein a 3/32 inch stainless steel ball requires one-half second to fall a distance of two inches in a 20 percent solution of the polymer - the solvent being substantially acetone.

2. Marketed by the Day-Glo Color Corp., Cleveland, Ohio, U.S.A. under the trademark of DAY-GLO Fluorescent Pigment Signal Green A-18. This material comprises about 96 percent by weight of a thermoplastic melamine-sulfonamide-formaldehyde resin prepared in accordance with Example 1, about 3 percent by weight of a daylight fluorescent green dye and about 1 percent by weight of a phthalocyanine green toner. This material has a minimum luminance factor of 55 percent, a minimum purity of 65 percent and a dominant wavelength of 540 to 547 millimicrons or nanometers determined in accordance with the daylight fluorescent color specification system described on pages 23 through 25 of the Day-Glo Color Corp. Technical Booklet No. 1170-A.

3. Marketed by the Monsanto Company, St. Louis, Missouri, U.S.A. under the trademark of Santicizer 3.

4. Marketed by E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware, U.S.A.

5. The above solvanted coating composition was prepared by mixing the melamine-sulfonamide-formaldehyde resin containing the sensible material and the methyl ethyl ketone in a 500 ml. Erlenmeyer flask with constant stirring thereby forming a composition having a uniform consistency. The cellulose acetate butyrate and the plasticizer were then added to the composition with constant stirring thereby forming a coating composition having a uniform consistency.

6. The solvanted coating composition was then coated onto 5 pound Jupiter paper tissue (20 in. x 30 in. x 480 sheets) and was uniformly spread over the tissue using a Meyer rod to a coverage of about 18 milligrams of solvanted coating composition per square inch of tissue. Jupiter paper tissue is a trademark for a 100 percent sulfite, fine parchment type tissue marketed by the Peter J. Schweitzer Division of Kimberly-Clark Corporation, Elizabeth, New Jersey, U.S.A. The methyl ethyl ketone was allowed to evaporate at room temperature thereby leaving a dried transferable coating composition having a thickness of about 0.2 to 0.3 mil on the tissue. The coated tissue was then cut into printing ribbons.

7. A green printing ribbon was then placed in a NCR Engineering Model Thermal Printer manufactured by The National Cash Register Company, Dayton, Ohio, U.S.A. The thermal printer printed a sequence of green marks on white bond paper. The print head of the thermal printer was operating at a temperature of about 250 to 300° C. and had a heated contact time with the transfer medium of about 10 milliseconds. The transferable coating composition was transferred to the white bond paper at a temperature of about 250 to 300° F.

8. The green marks printed on the white bond paper were tested for resistance to scratching and smudging by subjecting them to a thumb nail scratch and smudge test. In this test, a thumb nail was applied to the marks under pressure and was passed over the marks several times. The printed marks possessed excellent resistance to scratching and smudging upon visual examination.

9. In another test for thermal printability, a green printing ribbon was placed on white bond paper. A steel bar having a width of 1.5 inches and a thickness of 0.05 inch was heated to 300° F. and then applied by hand pressure to the backside of the transfer medium. The heated steel bar produced excellent marks on the white bond paper.

10. The green marks printed on the white bond paper were tested for resistance to scratching and smudging in the same manner as described above and the printed marks possessed excellent resistance to scratching and smudging upon visual examination.

11. It is claimed:

1. A thermal transfer medium comprising a base having a transferable coating composition thereon said coating composition comprising about 3 to 40 percent by weight of a cellulosic polymer; about 15 to 70 percent by weight of a thermoplastic aminotriazine-sulfonamide-aldehyde resin, said resin comprising the condensation product of at least one aldehyde selected from the group consisting of formaldehyde and paraformaldehyde, at least one aromatic monosulfonamide having two reactive amide hydrogens where the sulfonamido group is attached directly to the aromatic nucleus through the sulfur atom, and at least one aminotriazine having at least two amino groups, the amount of said aminotriazine being between about 17 and 50 mole percent of said monosulfonamide and the total amount of said aldehyde constituent being at least in excess of the total amount of said sulfonamide and aminotriazine constituents on a molar basis; about 3 to 40 percent by weight of a plasticizer; and about 1 to 45 percent by weight of a sensible material.

2. The transfer medium of claim 1 wherein the cellulosic polymer comprises cellulose acetate butyrate and is present in the coating composition in an amount of about 15 to 25 percent by weight.

3. The transfer medium of claim 1 wherein the aminotriazine component of the thermoplastic resin is melamine and said resin is present in the coating composition in an amount of about 50 to 65 percent by weight.

4. The transfer medium of claim 1 wherein the plasticizer is

present in the coating composition in an amount of about 15 to 25 percent by weight.

5. The transfer medium of claim 1 wherein the plasticizer is N-ethyl-p-toluenesulfonamide.

6. The transfer medium of claim 1 wherein said sensible material comprises a green dye or pigment.

7. The transfer medium of claim 1 wherein said sensible material comprises a red dye or pigment.

8. The transfer medium of claim 1 wherein said sensible material comprises a black dye or pigment.

9. The transfer medium of claim 1 wherein said sensible material comprises a magnetic metal or oxide thereof.

10. The transfer medium of claim 1 wherein said sensible material is invisible to the naked eye under ordinary light.

11. The transfer medium of claim 1 wherein the sensible material is present in the coating composition in an amount of about 2 to 20 percent by weight.

12. The transfer medium of claim 1 wherein said base is a thin material.

13. The transfer medium of claim 12 wherein said base is a polymeric material.

14. The transfer medium of claim 13 wherein said base is a film of polyethylene terephthalate.

15. The transfer medium of claim 12 wherein said base is a paper tissue.

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