

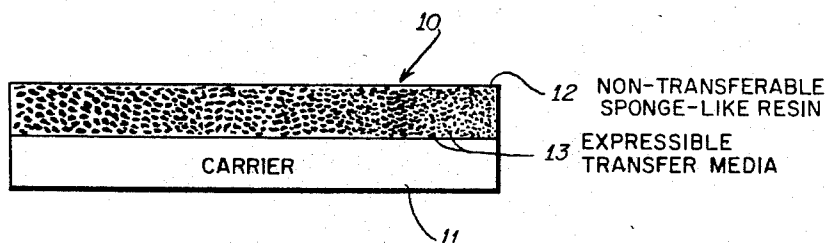
Nov. 22, 1966

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3,287,153

PRESSURE SENSITIVE SPONGE-LIKE TRANSFER DEVICE

Filed Aug. 22, 1963



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3,287,153 PRESSURE SENSITIVE SPONGE-LIKE TRANSFER DEVICE

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ments, to Royal Typewriter Company, Inc., New York,
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Filed Aug. 22, 1963, Ser. No. 303,914
4 Claims. (Cl. 117—36.1)

This invention relates to transfer devices of the type wherein a backing or carrier member is coated with a porous resinous non-transferable layer containing within its pores a pressure transferable marking composition; more particularly it relates to novel coating formulations having as the continuous phase high molecular weight polymer resins containing as the discontinuous phase a marking composition characterized by the inclusion of alkyl-aryl sulfonic acids, their metal salts and nitrogen derivatives.

Transfer devices employing coatings which comprise a porous resin as the continuous phase and an expressible marking vehicle as the discontinuous phase are well known in the art as exemplified by Australian Patent 10,136 of 1932. More recently polymer resins of vinyl configuration have been employed as the continuous phase in commercially available transfer devices.

The coatings on these transfer devices broadly comprise, after a solvent has been driven off by evaporation, a resin containing within its pores transfer media which comprises a transfer vehicle and coloring materials. These devices are popularly known as solvent coated transfer devices.

It has been found that the production of a solvent coated transfer device with a particular suitable resin requires more than routine experimentation. It requires the discovery of a transfer vehicle or vehicles suitable for use with a chosen resin in that a particular resin can retain or has a capacity to hold different amounts of different transfer vehicles. This limitation renders many transfer vehicles unsuitable for use with a particular resin since the resin-transfer vehicle ratio is controlling with respect to write characteristics and service as well as shelf life. Where the ratio is too high the amount of transfer vehicle expressed will be insufficient to produce a legible write; if the ratio is lowered a "dirty" write will be produced and the coating will be subject to offsetting as well.

In accordance with the invention coating compositions having relatively high resin-transfer vehicle ratios, on the order of 1/1 or greater, which include alkyl-aryl sulfonic acids, their metal salts and their nitrogen derivatives have been found which produce a "clear" legible write.

In accordance with the invention herein described a new polymer resin and transfer vehicles especially suited for use therewith in relatively high resin-transfer vehicle ratios has been found; said resins being characterized by their affinity to backing members such as paper and Mylar. Accordingly, an object of the invention is in the provision of a novel coating composition for solvent coated transfer devices.

Another object of the invention is in the provision of a coating composition including a resin suitable for use with any of a variety of transfer vehicle in ratios of resins

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to transfer vehicle which in the absence of additives in accordance with the invention would be too high to produce a legible write.

A further object of the invention is in the provision of a transfer coating having as the continuous phase a high molecular weight polymer resin and as the discontinuous phase transfer vehicles including alkyl-aryl sulfonic acids, their metal salts and their nitrogen derivatives and marking material.

A still further object of the invention is in the provision of a solvent coated transfer device employing the resins Exon 470 and Exon 471.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description.

Broadly, the coating formulation for a solvent coated transfer device in accordance with the invention comprises resins, solvents therefor, transfer media comprising transfer vehicles, coloring materials, and a compound comprising alkyl-aryl sulfonic acids, their metal salts and nitrogen derivatives.

While resins such as VYHH, copolymer of vinyl acetate and vinyl chloride may be used, the resins found to be particularly suitable in a solvent coated transfer device are those described in U.S. Patent Re. 24,206 and marketed by the Firestone Chemical Corporation under the names Exon 470 and Exon 471. In properly formulated resin-solvent solutions, hereinafter recited, these resins yield solutions of low viscosity which, after the solvents are released, produce films having the requisite flexibility, elasticity and hardness and which adhere well, without resort to intermediate binding layers, to surfaces having widely divergent characteristics such as paper and polyethylene terephthalate (Mylar) as well as others such as cellophane, polycarbonate and other materials used in carbon papers and ribbons.

As disclosed in Re. 24,206 the Exon resins employed in the invention comprise vinyl chloride interpolymer resins formulated as follows; the percentages cited all being on the basis of the total weight of the resin.

	Percent
Vinyl chloride	55-75
A dihydrocarbon maleate, chloromaleate or fumarate containing 6-24 carbon atoms, or a mixture of esters of this type	14-35
A monohydrogen monoalkyl maleate, chloromaleate, or fumarate containing 5-14 carbon atoms, or a mixture of esters of this type	5-10
Trichloroethylene	1.5-6.5

Solvents suitable for dissolving the Exon resins may be such as are used in the lacquer manufacturing field such as aliphatic ketones and esters, etc.

The transfer vehicles comprise non-drying low vapor pressure vehicles, like oils, greases or solids, characterized in that they are non-solvents or at best partial solvents for the resins but are compatible with the properly formulated resins-solvent solution. Examples of such vehicles are natural products such as some vegetable and animal oils and their treated products such as polymerized and epoxidized oils, some fatty acids and their derivatives, some derivatives of other organic acids like behenic, citric

or dodecyl benzene sulfonic acid, long chain alkyl alcohols and particularly paraffinic mineral oils.

The coloring material added to the transfer vehicles to produce the transfer media or discontinuous phase of the coating composition, as will be appreciated by those skilled in the art, are either dyes which are soluble in high boiling organic fluids such as triphenylmethane dyes, azo dyes, diazine dyes, or basic anthraquinone dyes, or organic pigments, toners, and lakes, particularly those made utilizing aromatic polyhydroxy compounds, milori blues, carbon blacks, graphites, iron oxides, metal powders and other inorganic pigments.

In accordance with the invention the inclusion of alkyl-aryl sulfonic acids, their salts or nitrogen derivatives permit compositions with a resin to transfer vehicle ratio on the order of 1/1 which produce a legible, distinct, and "clean" write. When the transfer vehicles include a salt of a sulfonic acid e.g. sulfonates such as barium, sodium, calcium, magnesium, etc., dissolved in a fluid such as mineral oil, a marked improvement in the write, particularly when the resin Exon 470 is used, was obtained by adding to the composition acids such as ethyl acid phosphate, hydrochloric acid, phosphoric acid and others. In formulations which do not contain the salt of a sulfonic acid but rather a straight alkyl-aryl sulfonic acid added to transfer vehicles such as mineral oil, nabob oil, blown rapeseed oil, etc., by some chemical mechanism not fully understood, the release of the transfer media was promoted, thereby to produce a legible write, which, in the absence of the sulfonic acid, would not produce a write.

Additives, other than the acid additives to improve release characteristics of transfer media which would otherwise not release sufficiently to produce legible writes, to improve the quality of the compositions, such as fillers, grinding agents, anti-oxidents for the oils and stabilizers for the polymers, may also be added.

Alternative to the coloring material, the transfer vehicles may include materials to render the coating suitable for electrophotographic magnetic or thermographic applications.

In accordance with the invention, the coloring materials and the transfer vehicle are mixed together and ground in a roller mill. The polymer resins are then dissolved in solvents and mixed with the transfer media, the acid additives and others are added, and the entire composition is ground for several hours in a ball mill.

The composition may then be applied to a carrier member by roller coater or equivalent conventional apparatus. The transfer sheet is illustrated in the single figure of the drawings. The thickness of the coating as well as that of the carrier depends on the end use; for general use as a transfer sheet the thickness may be varied from .0005" to .00015". Upon evaporation of the solvent or solvents the resin settles to a sponge-like substance containing in the pores thereof the transfer media expressible therefrom only in response to pressure, impact forces or heat.

Examples of transfer compositions in accordance with the invention which when the solvent was driven off produced a coating which adhered well to paper and Mylar as well as other materials are given below. The amounts of ingredients cited being given as parts by weight.

Example I—		Parts by weight
Resin:		
Exon #470	-----	42.6
Solvent:		
Methyl ethyl ketone (MEK)	-----	85.5
Toluol	-----	85.5
Transfer Vehicle:		
30% barium sulfonate in mineral oil	-----	40.5
Coloring:		
Black pigment #8962	-----	14
Crystal violet	-----	.5

Example I—Continued		Parts by weight
Acid Additive:		
5% ethyl acid phosphate in MEK	-----	20
Behenic acid	-----	2
Other Additives:		
Yelkin TTS	-----	.26
Syloid #244	-----	.8

Example II—		Parts by weight
Resin:		
Exon #470	-----	40.0
Solvent:		
MEK	-----	160.0
Transfer Vehicle:		
30% barium sulfonate in mineral oil	-----	40.5
Color:		
Black pigment #8962	-----	18.1
Acid Additives:		
Tannic acid	-----	1.1
5% ethyl acid phosphate in MEK	-----	20
Other Additives:		
Yelkin TTS	-----	.3

Example III—		Parts by weight
Resin:		
Exon #470	-----	42.6
Solvent:		
MEK	-----	85.3
Toluol	-----	85.3
Transfer Vehicle:		
30% barium sulfonate in mineral oil	-----	42.6
Color:		
Black Pigment #8962	-----	13.6
Acid Additive:		
5% Hydrochloric acid in MEK	-----	19.2
Other Additive:		
Yelkin	-----	.2

Example IV—		Parts by weight
Resin:		
Exon #470	-----	30.8
Solvent:		
MEK	-----	123
Transfer Vehicle:		
30% isopropylamine sulfonate in mineral oil	-----	52.5
Color:		
Black Pigment	-----	15.8
Acid Additive:		
5% ethyl acid phosphate in MEK	-----	20
Other Additive:		
Yelkin TTS	-----	.3

Example V—		Parts by weight
Resin:		
Exon #470	-----	34.2
Solvent:		
MEK	-----	137
Transfer vehicle:		
30% barium sulfonate in mineral oil	-----	49.5
Color:		
Black pigment #8962	-----	10.0
Carbon black	-----	5.0
Acid Additive:		
Tannic acid	-----	1.0
5% ethyl acid phosphate in MEK	-----	20
Other additive:		
Yelkin TTS	-----	.3

Example VI—		Parts by weight
Resin:		
Exon #470	-----	42.6
Solvents:		
MEK	-----	85.3
Toluol	-----	85.3

Example VI—Continued		Parts by weight
Transfer Vehicle:		
30% barium sulfonate in mineral oil	----	37.6
Color:		
Black pigment #8962	-----	13.6
Acid Additive:		
5% hydrochloric acid in MEK	-----	19.2
Other Additives:		
Yelkin TTS	-----	.2
Carnauba wax	-----	5

Example VII—		Parts by weight
Resin:		
Exon #470	-----	42.6
Solvent:		
MEK	-----	85.3
Toluol	-----	85.3
Transfer Vehicle:		
30% barium sulfonate in mineral oil	-----	42.6
Color:		
Alkali blue	-----	13.6
Acid Additive:		
10% hydrochloric acid in MEK	-----	19.2
Other Additive:		
Yelkin TTS	-----	.2

Example VIII—		Parts by weight
Resin:		
Exon #471	-----	42.6
Solvent:		
Toluol	-----	85.3
MEK	-----	85.3
Transfer Vehicle:		
30% barium sulfonate in mineral oil	-----	42.6
Color:		
Black pigment #8962	-----	13.6
Acid Additive:		
10% hydrochloric acid in MEK	-----	19.2
Other Additive:		
Yelkin TTS	-----	.2

Example IX—		Parts by weight
Resin:		
Exon #471	-----	46.5
Solvent:		
Toluol	-----	93
MEK	-----	93
Transfer Vehicle:		
60% sodium petroleum sulfonate in mineral oil	-----	6.15
Bayol oil	-----	31.5
Color:		
Black Paste	-----	.69
Black pigment #8962	-----	10.39
Peerless black pigment	-----	3.46
Purple dye	-----	1.33

In the Exon 470 Formulas I-VIII which employ transfer vehicles comprising a sulfonate dissolved in mineral oil, an acid additive such as hydrochloric and ethyl acid phosphate improved the write. It is to be understood however that the use of the sulfonate alone, particularly with Exon 471 as shown in Example IX, produced a legible write in the resin to softener ratios given i.e. on the order of 1:1. In the above formulations the 30% barium sulfonate dissolved in mineral oil is marketed by the Bryton Chemical Co. as barium sulfonate 30-N; the isopropylamine is a 30% solution of a synthetic amine-sulfonate in mineral oil also marketed by Bryton Chemical Co.

The Yelkin TTS is a lecithin (phosphatide) which aids grinding. Syloid #244 is a silica compound to increase the viscosity of the formulations.

While barium sulfonate 30-N is given in most of the composition formulas as the transfer vehicle, it is to be understood that sodium, calcium and other metal sulfonates from the alkyl-aryl sulfonic acids or their

nitrogen derivatives dissolved in mineral oil or equivalent would also serve.

Example X—		Parts by weight
Resin:		
Exon #470	-----	42.2
Solvent:		
MEK	-----	84.2
Toluol	-----	84.2
Transfer Vehicle:		
Nabob oil	-----	42.2
Color:		
Black pigment #8962	-----	13.5
Acid Additive:		
30% sulfonic acid in mineral oil	-----	2.1
Other Additive:		
Yelkin TTS	-----	.2

Example XI—		Parts by weight
Resin:		
Exon #470	-----	46.2
Solvent:		
MEK	-----	82.2
Toluol	-----	82.2
Transfer Vehicle:		
Nabob oil	-----	44.2
Color:		
Black pigment #8962	-----	12.5
Acid Additive:		
30% sulfonic acid in mineral oil	-----	2.1
Other Additive:		
Yelkin TTS	-----	.2

Example XII—		Parts by weight
Resin:		
Exon #470	-----	42
Solvent:		
MEK	-----	84
Toluol	-----	84
Softener:		
Blown rapeseed oil	-----	16.5
Color:		
Black pigment #8962	-----	13.4
Acid Additive:		
30% sulfonic acid in mineral oil	-----	27.8
Other Additive:		
Yelkin TTS	-----	.2

Formulas X-XII are examples of formulas which utilize transfer vehicles which do not contain a sulfonate. In these formulas the sulfonic acid solution marketed by Bryton Chemical Co. as sulfonic acid #45 supplies the sulfonic acid compound as well as the acid to produce a transfer coating which releases the marking material readily to produce a legible write.

It should be understood that the foregoing disclosure relates to only a preferred embodiment of the invention and that it is intended to cover all changes and modifications of the example of the invention herein chosen for the purposes of the disclosure which do not constitute departures from the spirit and scope of the invention.

The invention claimed is:

1. A pressure sensitive transfer sheet comprising a flexible carrier member having a sponge-like non-transferable resinous layer, and transfer media releasably retained in the pores of said resinous layer, said transfer media comprising a non-drying low vapor pressure fluid, said resinous layer comprising a resin having

	Percent
Vinyl chloride	55-75
A dihydrocarbon maleate, chloromaleate or fumarate containing 6-24 atoms of carbon or a mixture of esters of this type	14-35
A monohydrogen monoalkyl maleate chloromaleate or fumarate containing 5-14 carbon atoms or a mixture of esters of this type	5-10
Trichloroethylene	1.5-6.5

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said resin and fluid being in a ratio of substantially 1:1 by weight, said transfer media including a quantity of an alkyl-aryl sulfonic compound and a quantity of coloring material.

2. A sheet as recited in claim 1 wherein said compound comprises an alkyl-aryl sulfonate dissolved in said fluid.

3. A sheet as recited in claim 1 wherein said compound comprises an alkyl-aryl sulfonic acid added to said fluid.

4. A sheet as recited in claim 1 wherein said alkyl-aryl

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sulfonic compound is barium sulfonate and further wherein said fluid includes a quantity of acid.

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MURRAY KATZ, *Primary Examiner.*