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PRESSURE-SENSITIVE ADHESIVE WEB PRINTED ON BACK WITH TRANSFER-PROOF INK

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ABSTRACT OF THE DISCLOSURE

A transfer-proof ink particularly suitable for printing on the backing of pressure-sensitive adhesive webs such as tapes, said ink containing a compatible transfer-proofing agent soluble in the ink solvent but substantially insoluble in both backing and adhesive layers of web. The invention includes pressure-sensitive webs which have printed matter on the non-adhesive side of said webs and which can be wound and unwound in the usual manner without transfer of either ink or adhesive to the adjacent side, the printed matter of said webs being formed from the transfer-proofing ink of this invention.

BACKGROUND OF THE INVENTION

Pressure-sensitive adhesive webs are well-established articles of commerce. In the form of tapes of varying width they are used to perform many functions including joining, mending, masking, sealing, splicing, protecting, reinforcing, identifying and decorating. Webs of larger width are often employed as coverings for walls and the like. A common procedure in handling a pressure-sensitive adhesive web is to wind it up in a roll with adjacent contact between adhesive-coated and adhesive-free sides, the web being unwound thereafter before use. In order to facilitate unwinding such a roll, the backing is usually coated with an appropriate "low adhesion" or release coating.

In many applications of pressure-sensitive webs, it is desirable to have a printed message or design on the adhesive-free backing of the web. When commonly available inks are used for such printing, a difficulty is encountered which arises from the tendency of the print to transfer to the adjacent adhesive-coated side when the web is unrolled, particularly if the printed web is retained in roll form for prolonged periods of time or at elevated temperatures. The adhesion of ink to backing frequently is so strong that the web breaks when an attempt is made to unroll it. This is particularly the case when highly aggressive adhesives are used. In some instances adhesive separates from the backing and transfers onto the print.

When it is attempted to overcome the aforementioned deficiencies by reducing the adhesive level of the pressure-sensitive adhesive, the usefulness of the product is seriously limited to applications which require only low bond strength. For example, adhesive tapes intended for reinforcing, joining or splicing would not be satisfactory if made in this manner.

Attempts have also been made to modify the ink by the addition of natural or synthetic waxy materials, but such procedures have been unsatisfactory because such additives tend to migrate into the adhesive layer and cause a variety of deficiencies such as detackification and loss in cohesive strength.

Another approach is to subject the printed web, before rewinding, to an additional coating with an appropriate release agent but this involves cumbersome modifications in printing machinery and increased manufacturing costs.

SUMMARY OF THE INVENTION

A transfer-proof ink for printing on the backing of a pressure-sensitive adhesive web has now been found which makes possible winding and unwinding the printed web in the usual manner without transfer of either ink or adhesive to the adjacent side. Briefly state, the present invention comprises incorporating in the ink a compatible transfer-proofing (i.e., transfer-withstanding) agent soluble in the ink solvent but substantially insoluble in both backing and adhesive layer of the web.

Preferably, the ink of this invention contains: from about 15%–40% and preferably 18%–30% of a resinous binder; from about 0.5% to 25.0% and preferably 1% to 15% of a coloring agent which can be inorganic or organic; from about .01%–20% and preferably 0.1%–10% (of the dry ink solids) of the transfer-proof agent of this invention; and from about 15%–85% and preferably 45%–80% of a solvent for said resinous binder and the transfer proof agent. Additional ingredients such as conventional ink modifiers can be added to this ink composition. Preferred inks to which the transfer proof agents of this invention can be added, are the flexographic inks. Such inks are described in pages 49–51 of the September 1966 issue of the Paper, Film and Foil Converter.

DETAILED DESCRIPTION OF THE INVENTION

Printing inks in general comprise coloring agents and liquid vehicles including solutions of suitable binders in solvents. As is well-known to those trained in the art, specific choice of binders and solvents depends on several factors; in particular, the nature of the coloring agents and the nature of the substrate to be printed. The essence of the instant invention comprises incorporating into such an ink a transfer-proofing agent which is soluble in the solvent of the ink and compatible with the ink components but which is insoluble in the substrate, namely the backing of a pressure-sensitive adhesive web, and also substantially insoluble in the adhesive layer of said web.

In a preferred embodiment of this invention, the ink is a type commonly called flexographic ink intended to be printed by the process well-known as a flexographic process. Flexographic inks are particularly useful in printing on cellulosic substrates such as cellophane, paper, cotton cloth and the like and on certain types of plastic film including polyvinyl acetate, polyvinyl alcohol, polyesters and polyolefins and also on certain metal foils such as aluminum foil.

Solvent systems commonly employed in the manufacture of flexographic inks are the lower aliphatic alcohols, including propanol, isopropanol, ethanol and butanol; the lower aliphatic esters, in particular ethyl acetate and the lower aliphatic ketones, in particular methyl ethyl ketone. The amount and type of solvent are regulated so as to give the ink the desired drying speed and degree of penetration.

Binders for ink vehicles are commonly selected from rosin esters, synthetic film-forming polymers, polyamides, alkyd resins and proteins, including casein, gelatin and soy protein. The choice of binder depends upon the particular substrate used, each type of fibrous or film material having specific requirements for optimum adhesion, as is known to those trained in the art.

In addition to the above-mentioned chief components, flexographic inks customarily contain various amounts of modifying agents selected from waxes such as beeswax or paraffin wax, drying oils such as linseed oil, castor oil, turpentine oil, menhaden oil or the salts of linoleic acid, eleostearic acid and the like with amines such as triethanolamine or hydroxypropylamine, as well as small quantities of so-called drier like cobalt resinate, cobalt linoleate or an aluminum soap of linseed or tung oil. The use of such modifying agents is a well-established art.

Pressure-sensitive adhesives referred to herein are conventional and comprise elastomers such as natural or synthetic rubbers, tackifying resins, plasticizers, fillers and curing agents.

Materials which are suitable as the transfer-withstanding agent of this invention include (a) surface active compounds whose non-polar part comprises polyfluorinated alkyl groups and (b) complexes of fatty acids or aceto-acetic acid or acetoacetic acid esters, with aluminum, chromium or titanium.

The fluorinated surface active compound can be anionic, cationic or nonionic. The polyfluorinated alkyl groups therein can contain between 3 and 21 carbon atoms, alkyls with from 7 to 11 carbon atoms being preferred. The hydrogens of the alkyl can be completely replaced by fluorine atoms or they can be partially so replaced. For best results it is preferred that at least about three-fourths of the hydrogen on the alkyl be replaced by fluorine.

Examples of nonionic types are alcohols, ethers, amines and esters. Thus, when the alkyl group is perfluorononyl, for example, the compound can be perfluorononyl alcohol, perfluorononyl methyl ether, the 2-methoxyethylether of perfluorononyl alcohol, perfluorononylamine or perfluorononyl acetate or other analagous compounds. In particular, nonionic types of fluorinated surfactants include 1H, 1H, 7H-dodecafluoro-1-heptanol; 1H, 1H, 9H-hexadecafluoro-1-nonanol; 1H, 1H, 11H eicosafluoro-1-undecanol, 1H, 1H, 9H-hexadecafluoro-1-nonyl acetate and, 1H, 1H, 11H eicosafluoro-1-undecyl butyrate.

Examples of cationic types are substituted ammonium compounds as perfluorononyl ammonium chloride, polyfluoroundecanyl trimethyl ammonium bromide, polyfluorononyl triethanolammonium acetate or N-polyfluoroheptanyl 2-hydroxy propylammonium carbonate.

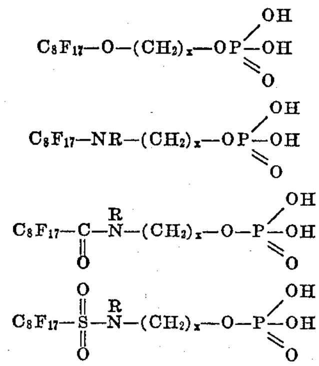
Examples of anionic types of fluorinated surface active compounds are polybasic acids which are partially esterfield by a polyfluorinated alcohol such as the monoesters of sulfuric acid, succinic acid, malic acid, fumaric acid, adipic acid, oxalic acid or itaconic acid; or the mono- or bis-esters of phosphoric acid or citric acid. Specific examples of such substituted acids are mono-polyfluorononyl sulfate, mono-polyfluorolauryl succinate, mono-polyfluorostearyl adipate, mono-polyfluorononyl oxalate, mono - polyfluorononyl phosphate, bis - polyfluorononyl phosphate, 3-perfluoroethyl perfluorononyl phosphate and bis-polyfluorononyl citrate.

Said substituted acids can be totally or partially neutralized with the hydroxides of alkali metals or substituted ammonium ions to form the corresponding salts. They can likewise be reacted with ammonia, amines and substituted amines. The salts may be formed either before addition to the ink, or the polyfluoro alkyl derivative of the acid and the neutralizing base may be added separately to the ink and mixed therein to form the salt in situ.

Specific examples of such salts are sodium polyfluorononyl sulfate, potassium polyfluorolauryl succinate, ammonium polyfluorostearyl adipate, hydroxypropylammonium polyfluorononyl oxalate, triethanolammonium monopolyfluorononyl phosphate, hydroxypropylammonium bispolyfluorononyl phosphate, tetramethyl ammonium 3-perfluoroethyl perfluorononyl phosphate and triethanol ammonium bispolyfluorononyl citrate.

Other examples of anionic types of the fluorinated surface active compounds of this invention are those in which a polyfluorinated alkyl group is directly attached to the carbon, sulfur or phosphorus atom of respectively a carboxyl, sulfonate or phosphonate group. Thus the compound can be perfluoropelargonic acid, potassium perfluoropelargonate, triethanolammonium polyfluorononyl sulfonate and hydroxypropylammonium lauryl phosphonate.

The surface active transfer-proofing agent of this invention can have its polyfluorinated alkyl group attached to the polar end of the molecular via a connecting moiety such as an ether linkage, an amino linkage, a carbamido linkage or a sulfamido linkage. Thus for example, if the alkyl group is perfluorinated octyl and the polar end of the molecule is phosphate, the agent can be selected from compounds having the following structures:



wherein

x can be 1, 2, 3 or 4,

R can be hydrogen or an alkyl group having from 1 to 4 carbon atoms, and

either one or both of the hydrogen atoms of the phosphate moiety can be replaced by a cation resulting from neutralization by a suitable base as above described, forming the corresponding salt. A particularly useful example of an agent of this class is a product available commercially from Minnesota Mining and Manufacturing Corporation under the proprietary name FC–807 and identified by these suppliers as N-ethyl 2-perfluoroalkyl sulfonamide ethyl phosphate.

Commercially available chelate compounds derived from acetoacetic acid include a titanium chelate of acetylacetonate sold by E. I. du Pont de Numours and Co. as Tyzor AA, and an ethyl acetoacetate modified aluminum isopropylate available from the Harshaw Company as Compound PEA–1.

Substances from all the abovementioned categories can be applied either singly or in combination in preparing the transfer-proofing agent of this invention.

When a mixture is used, the components of the mixture can be added separately to the ink or when convenient said components can be mixed together before being added to the ink. The total solids of transfer-proofing agent can be used in amount from about 0.01 to 20 parts per 100 parts by weight of dry ink solids. Preferred amounts are in the range of between about 0.1 to 10 parts per 100 parts of dry ink components and more particularly in the range of from about 0.8 to 6.0 parts per 100 parts of dry ink solids.

As to the aforementioned metal complexes, these can be selected from aluminum, chromium and titanium Werner-type complexes respectively with fatty acids containing between 12 and 24 carbon atoms, preferably between 14 and 18 carbons, and from chelate compounds of said metals with acetoacetic acid and its C_2 to C_8 alkyl esters. Said fatty acids may have all or part of their hydrogens replaced by fluorine. Commercially available examples of said Werner complexes include the well-known Quilon series in which stearic acid, myristic acid and the like are coordinated with chromium, also the product available from E. I. du Pont de Nemours and Co. as Product A–101 and stated by these suppliers to be an aluminum complex with myristic acid, and the chromium complex of fluorine-containing fatty acid manufactured by Minnesota Mining and Manufacturing Corporation as product FC–806.

Although the transfer-proof inks of this invention are particularly suitable for printing on the backs of pressure sensitive tapes, they can be used for printing on substrates such as mentioned hereinbefore for pressure sensitive tapes, e.g. cellulosic substrates or polyolefin films, but which do not contain pressure sensitive adhesives, release coats and the like. Thus in printing of paper that is stacked up, one gets sticking in between sheets, especially when such sheets are piled up high and under heavy pressure and left in stacks for a long time. The incorporation of the transfer proofing agents of this invention in such inks fairly eliminates the sticking problem. Illustratively, the composition of Example 7 can be printed directly on cellophane, paper and aluminum foil. The ink shows decreased sticking qualities as compared with such ink without the transfer-proof agents of this invention.

This invention will be further described in connection with the following examples of the practice of it which are set forth for the purpose of illustration only and wherein proportions are in parts by weight unless specifically stated to the contrary.

Example 1

A flexographic ink was prepared using the following formulation, the amounts being expressed in parts by weight.

Nitrocellulose	25.0
Castor oil	10.5
Carbon black	6.5
Paraffinic wax	2.5
Cobalt naphthenate	0.5
Ethanol	28.0
Ethyl acetate	27.0
	100.0

This printing ink did not include the transfer-proofing agent of this invention.

Example 2

To 200 grams of the ink of Example 1 there was added 30 grams of a 10% solution in isopropanol of Quilon C, a Werner type fatty acid chromium complex supplied by E. I. du Pont de Nemours & Co.

This printing ink has the benefit of the transfer-proofing agent of this invention.

Example 3

The inks of Examples 1 and 2 were compared as the final coat on the backside of a commercial reinforced paper strapping tape previously coated, as is customary, with a release coat. This release coat comprised a 50/50 blend of a non-ionic aqueous emulsion of a thermoplastic acrylic polymer having a specific gravity of 1.15 and a minimum film formation temperature of 42° F. with an aqueous emulsion of a polyvinyl chloride resin having a specific gravity of 1.36 and a minimum film formation temperature of 190° F.

The adhesive of the tape used was compounded of the following ingredients:

	Parts by weight
Natural rubber (Mooney 55)	100
Zinc oxide	5
Polyterpene resin, M.P. 115° C.	90
2,5-ditertiary amyl hydroquinone	2
Accelerators:	
Dipentamethylene thiuramtetrasulfide	0.5
Zinc dimethyldithiocarbamate	2

and was coated from a 24.5% solution in toluene having an average viscosity of 20,000 cps.

The respective inks were printed on different samples of this commercial tape using a conventional laboratory flexographic printing machine. In each case, the printed tape was dried under infrared radiation and rewound in the usual manner.

Samples of the printed rolls were aged for twelve days, both under room temperature conditions and also in an

oven at 120° F. After these two types of aging, the respective tapes were unwound at high speed.

In case of the rolls printed with the ink of Example 1, both the shelf-aged and oven-aged samples showed considerable ink transfer to the adhesive and the ink remaining on the backing was fuzzy and had poor definition. Ink transfer was so great that no measurement of unwind force was made.

In sharp contrast were the result obtained in the case of the rolls printed with the ink of Example 2, incorporating the transfer-proofing agent of the instant invention. No transfer of ink was noted in either shelf-aged or oven-aged rolls. It was furthermore found that the unwind force at high speed exhibited by both types of aged samples was 85 oz./in., a value which is characteristic of unprinted rolls.

Example 4

To 200 grams of the ink of Example 1 there was added 30 grams of a 10% solution in isopropyl alcohol of Zonyl RP available commercially from E. I. du Pont de Nemours & Co. and stated by them to be the triethanolamine salt of mono- and bis-perfluoroalkyl phosphate. This ink, thus modified by the method of the instant invention, was printed and tested as in Example 3. The shelf-aged rolls showed no ink transfer and had a high-speed unwind force equal to 45 oz./in. While the oven-aged rolls showed some adhesive transfer onto the surface of the ink, there was marked improved over the condition exhibited in the case of the unmodified ink of Example 1.

Example 5

To 200 grams of the ink of Example 1 there was added 5 grams of a 10% solution in isopropyl alcohol of Zonyl RP and 20 grams of a 10% solution in isopropanol of Quilon C. Tests carried out in the manner of the previous examples showed no transfer for either shelf-aged or oven aged rolls.

Example 6

To 200 grams of the ink of Example 1 there was added 25 grams of a 5% solution in isopropanol of a product designated as FC 806, available commercially from Minnesota Mining and Manufacturing Corporating and stated by these suppliers to be a chromium complex of a fluorine-containing fatty acid. The ink containing this transfer agent showed minimum transfer on to the adhesive.

Example 7

To 200 grams of ink of Example 1 there was added 20 grams of 10% solution in ethanol of a titanium chelate of acetylacetonate available commercially from Du Pont as Tyzor AA. The ink showed advantageous non-transfer properties as in Example 2 in spite of the lower amount of additive. The unwind force at high speed was 85 oz./in. for aged roll samples.

Example 8

To 200 grams of ink of Example 1 there was added 50 grams of a 10% solution in ethanol of an ethyl acetoacetate modified aluminum isopropylate commercially available from Harshaw Chemical Company as Aluminum Chelate PEA-1. When printed on a cellophane backing this ink showed transfer onto the adhesive of clear Mylar pressure sensitive tape.

Example 9

To 200 grams of the ink of Example 1 there was added 50 grams of a 10% solution in ethanol of an aluminum complex of myristic acid marketed by Du Pont as Compound A-101. The additive showed good compatibility with the ink, which exhibited the advantageous properties of this invention.

Example 10

To 200 grams of the ink of Example 1 there was added 5 grams of a 10% solution in isopropanol of Quilon C and 5 grams of 10% solution in isopropanol of Compound A–101. This ink was printed on paper. Subsequent contact with the adhesive side of a conventional transparent pressure sensitive tape showed minimum or no transfer of the ink to the tape adhesive.

Example 11

This illustrates applying the method of this invention to a commercial pressure sensitive adhesive tape comprising a cellophane backing coated with a customary release coating. Two identical rolls of such commercial tape were found to have, before printing, an unwind force of 30 to 35 oz./in.

The two rolls were printed respectively with the inks of Example 4 and Example 1, using the method of Example 3.

The tape which was printed with the ink of Example 4, which is an ink of this invention, showed the same adhesion to backing as when the ink was absent, the unwind force being 30 to 35 oz./in. No transfer of ink was noted and the ink definition remained excellent. After aging, the results were even more dramatic, there being still no evidence of transfer and ink definition still remaining excellent. Furthermore, the unwind force of the aged samples was within the range of the correspondingly aged unprinted sample.

In contrast, the tape which was printed with the ink of Example 1 and which did not have the benefit of this invention, had an unwind force before aging equal to 65 oz./in. This higher adhesion to backing resulted in partial transfer of ink to adhesive as well as poor fuzzy definition of the ink image. After aging the unwind force was increased beyond that of the correspondingly aged unprinted sample, and the transfer of ink was so great that ink definition was very poor.

Example 12

The ink of Example 1 was printed on a highly adhesive reinforced plastic film tape. The unwind force was found to be only 25 oz./in. as compared to 65 oz./in. obtained by printing on another sample of the same type with the ink of Example 2. After aging for 12 days at 120° F., the unwind force of the product comprising the transfer-proofing agent of this invention increased to only 50 oz./in. as compared to 100 oz./in. with the product not containing said agent. After unwinding, the product made without transfer-proofing agent had poor ink definition and showed considerable transfer of ink to the adhesive layer. The product made with transfer-proofing agent, on the other hand, peeled without observable transfer and ink definition was excellent.

Example 13

This example illustrates the negative effect obtained when a synthetic wax is used in place of the transfer-proofing agent of this invention. To 200 grams of the ink of Example 1, there was added 50 grams of a 10% solution in ethanol of Carbowax 300, a polyethylene glycol supplied by Union Carbide. This ink was printed and tested as in Example 3. In sharp contrast to the results with this invention's inks of Examples 1 and 2, heavy ink transfer was observed in case of both shelf-aged and oven-aged rolls, and the aged samples showed drastic detackification. The high-speed unwind force of both types of aged rolls was 120 oz./in., which was 50% higher than was obtained with the unprinted rolls and with the rolls printed with the Example 2 ink of this invention.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A pressure-sensitive adhesive web having transfer-proof printed matter on the backing thereof, said printed matter being the dry solid deposit from a liquid ink containing as conventional components from about 0.5 to 25% of coloring agent, from about 15–40% of a resinous binder and from about 15–85% of a solvent selected from ethanol, propanol, isopropanol, butanol, the lower aliphatic esters and the lower aliphatic ketones, and also containing, as an improvement, about 0.01%–20%, based on dry ink solids, of a transfer-proofing agent selected from the Werner-type complexes of aluminum, chromium and titanium with fatty acids containing between 12 and 24 carbon atoms, complexes of said metals with derivatives of said fatty acids having all or part of their hydrogens replaced by fluorine, and chelate compounds of said metals with acetoacetic acid and its C_2 to C_8 alkyl esters.

2. The web of claim 1, wherein the transfer-proofing agent is an aluminum complex of myristic acid.

3. The web of claim 1, wherein the transfer-proofing agent is a Werner complex of chromium with a mixture of myristic and stearic acids.

4. The web of claim 1, wherein the transfer-proofing agent is titanium chelate of acetylacetonate.

5. The web of claim 1, wherein the transfer-proofing agent is an ethyl acetoacetate modified aluminum isopropylate.

6. A pressure-sensitive adhesive web having a transfer-proof ink imprint printed on the backing thereof, said ink being a conventional flexographic ink improved by the addition thereto of about 0.01%–20%, based on dry ink solids, of a transfer-proofing agent selected from the Werner-type complexes of aluminum, chromium and titanium with fatty acids containing between 12 and 24 carbon atoms, complexes of said metals with derivatives of said fatty acids having all or part of their hydrogens replaced by fluorine and chelate compounds of said metals with acetoacetic acid and its C_2 to C_8 alkyl esters.

7. A roll of pressure sensitive tape, having a pressure sensitive adhesive on one side of said tape and printed matter on the other side thereof, said other side thereof being in contact with pressure sensitive adhesive of the adjacent winding of said roll and wherein the printed matter is formed from an ink containing as conventional components from about 0.5 to 25% of a coloring agent, from about 15–40% of a resinous binder and from about 15–75% of a solvent selected from ethanol, propanol, isopropanol, butanol, the lower aliphatic esters and the lower aliphatic ketones, and also containing, as an improvement, about 0.01%–20%, based on dry ink solids, of a transfer-proofing agent selected from the Werner-type complexes of aluminum, chromium and titanium with fatty acids containing between 12 and 24 carbon atoms, complexes of said metals with derivatives of said fatty acids having all or part of their hydrogens replaced by fluorine and chelate compounds of said metals with acetoacetic acid and its C_2 to C_8 alkyl esters.

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