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TRANSFER COATING AND PAPER

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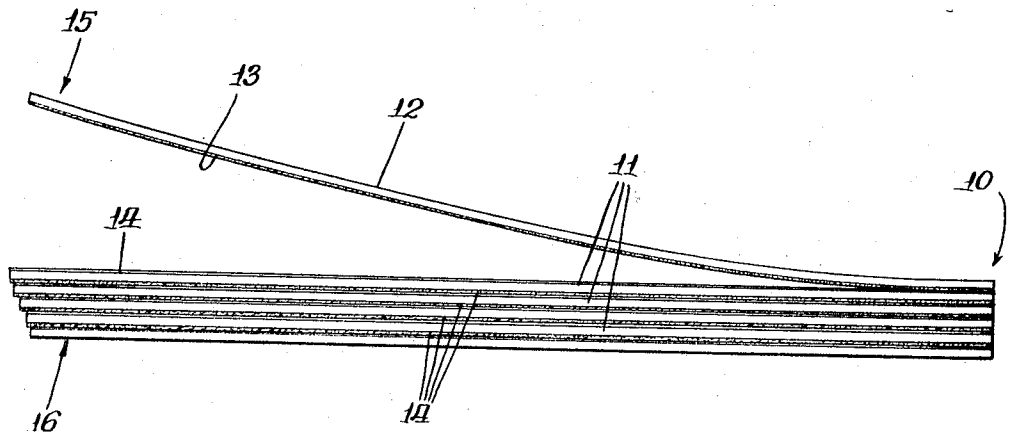

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TRANSFER COATING AND PAPER

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ABSTRACT OF THE DISCLOSURE

A transfer sheet having a release coating containing clay filler and a water-soluble binder base such as casein and further containing 5 to 30 parts by weight highly surface-active wetting agent per 2 to 10 parts by weight binder and in which the wetting agent is one which boils above the boiling point of water, such as a Pluronic or other non-ionic alkylene oxide-hydrophobic base condensation product. The wetting agent provides proper release properties for the coating while retaining the coating as a generally smudge-free coating.

THE DISCLOSURE

This invention relates to transfer coatings used on the reverse surface of a fibrous sheet, where the fibrous sheet is pressure transmitting and has a mark receiving front surface, so that the pressure of a mark impressed on the mark receiving surface will be transmitted through the sheet to reproduce the mark by transfer of the coating to a surface in backing facial contact with the coating. More particularly, this invention relates to transfer coatings for copying paper and to copying paper and manifolds thereof employing such coatings.

It has been known to provide copy paper of the type having transfer coatings in the form of backing coatings on writing paper and the like. Such coated sheets of paper are often provided in stacks or manifolded forms whereby a plurality of copies can be produced during the original writing or printing on the top sheet of the stack. The transfer coating performs the same general function as a sheet of carbon paper inserted between leaves of a stack of paper. Each sheet in the stack is capable of transmitting pressure from writing on the top sheet throughout the stack to produce good, clear copies on each successive sheet in the stack. It will be apparent that the greater the number of sheets in a manifold, the more pressure will be needed for writing, and a point will be reached where, under normal writing pressure, there is a limit to the number of sheets which can be used. Therefore, it is always desirable to improve transfer coatings for more distinct and legible copies with less pressure so that a greater number of sheets can be used in a manifold for a greater number of copies.

Another problem with respect to such transfer sheets relates to the balance of transferability and smudging of the transfer coating. Transfer coatings having greater transferability are usually more easily smudged, and coatings having lower smudge properties are usually low in transfer properties. It becomes necessary to balance desirable smudging and transfer properties, one usually at the expense of the other.

Another disadvantage with respect to many transfer coatings is that they are applied in the form of a solution in volatile solvent, often requiring provision for removal and/or venting of noxious fumes accompanied with expense in the loss of solvent and/or equipment for recovery of the solvent.

It is an object of this invention to provide a new and useful transfer coating for a copy sheet and to provide a copy sheet, or manifold of copy sheets, employing the coating.

Another object is to provide a new and improved copy sheet in which the transfer coating has good anti-smudge properties while retaining good transferability.

Still another object of this invention is to provide a transfer sheet according to any of the foregoing objects which can be stacked to a greater height, e.g. 10–20 sheets in a manifold, while still having good transferability and low smudge properties.

Yet another object is to provide a new and useful transfer coating composition for use in accordance with any of the foregoing objects which can be applied in a medium without necessity of using volatile organic solvents.

Other objects of this invention will be apparent from the following description and the drawing in which the figure is a schematic showing of an enlarged cross-section through a manifold **10** of copy paper sheets **11**.

While this invention is susceptible of embodiment in many different forms, there is shown in the drawings and will herein be described in detail a specific embodiment of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the invention to the embodiment illustrated.

Referring to the drawing in more detail, each of the copy paper sheets **11** includes a sheet of writing paper **12** which is pressure transmitting with respect to ordinary writing pressure and has a transfer coating **13** on its lower or reverse surface and a receptor coating **14** on its upper or obverse surface. The top cover sheet **15** of the illustrated manifold and the bottom sheet **16** of the manifold can be identical to sheets **11**, or the receptor coating **14** and transfer coating **13** can be omitted from sheets **15** and **16** respectively. The transfer sheets of the illustrated manifold **10**, as described herein, function as one-time transfer sheets and are not intended for reuse as a reusable carbon paper.

The transfer coating **13** is applied in a coatable aqueous liquid form. The water is then removed by vaporization to leave the transfer coating on the surface of the sheet **12**. In addition to sufficient water to provide a coatable composition, the coating composition includes a water-miscible binder, a normally liquid, water soluble, surface-active wetting agent which boils above the boiling point of water so that it is not removed during vaporization of the water, a pigment and a finely divided filler such as a clay filler, usually kaolin. The pigment is included to impart the desired shade or color to the transfer coating and the filler is for the purpose of bodying the transfer coating, i.e. providing the transfer coating with transfer consistency after evaporation of the water. Examples of suitable pigments include titanium dioxide, carbon black, iron blue, phthallocyan blue, napthol red and other normally solid color materials.

In coating compositions for forming transfer coatings having good anti-smudge and transfer properties, the composition will usually include a binder and wetting agent in a ratio of from about 2 to about 10 parts by weight of the binder, dry basis, to each 5 to 30 parts by weight of the wetting agent. It is preferred that the total coating composition contain from 2 to 10 weight percent binder and from about 5 to about 30 weight percent wetting agent.

The binder may be any water soluble, adhesive material. Specific examples include, but are not limited to, casein, polymeric carbohydrates, protein binders of the natural glue type, and the water soluble synthetic polymeric resins such as polyvinylalcohol, polyvinylethermaleic anhydride resin, methylcellulose, and the like.

The wetting agent may be any surface-active wetting agent and functions in combination with the binder to permit release of the transfer coating under writing pressure. The wetting agent may also function as a plasticizer

in the film of transfer coating after evaporation of water. The binder and wetting agent are balanced to provide good transfer properties as well as good anti-smudge properties. Increasing the amount of binder or decreasing the amount of wetting agent decreases both transferability and smudging, while decreasing the amount of binder and increasing the amount of wetting agent increases both transferability and smudging. Thus, the compositions of this invention can be balanced depending upon the property desired.

Specific examples of suitable surface-active wetting agents are those organic water soluble compounds having a structure including an ethylene oxide group, i.e. $-CH_2CH_2O-$, and those organic compounds selected from the group consisting of water soluble sulfonates, sulfates, ditertiary acetylenic glycol, and C_8 to C_{22} fatty acid salts of N-fatty alkylene diamines. Such wetting agents are well known in the art and are commercially available. The preferred wetting agents are those including the ethylene oxide group described above, and especially preferred are the ethylene oxide-propylene glycol condensation products such as Pluronics L–44, L–62 and L–64, which are available from Wyandotte Chemicals Corp. The Pluronics are high molecular weight nonionic surfactants prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene alcohol and are conventionally referred to as ethylene oxide-polypropylene glycol condensation products.

When using certain binders in compositions of this invention, the binder may not be soluble in the presence of certain wetting agents. Such insolubility is apparently due to a pH imparted to the aqueous solution which is incompatible with retaining the binder in solution or intimate dispersion. For example, when casein is used as a binder, the pH of the wetting agent should preferably be above 7 to keep the casein in solution while, when polyvinylalcohol or other binders are used, the pH can be acidic or basic.

In the coating compositions, the ingredients mixed together are not chemically reactive with each other to any extent destroying their functions as binder, wetting agent, filler and pigment; and the compositions all appear to be physical mixtures of the ingredients. Other additives in addition to those materials described above can be used, including water soluble antioxidants, bactericides, fungicides, etc.

In the use of sheets having a transfer coating according to this invention, the entire composition of the coating transfers, i.e. the transferred material on the receptor surface will include each ingredient of the original transfer coating generally in the same proportion as before transfer. The binder does not function as a matrix from which a pigment can be carried but actually transfers to the receptor surface and carries the pigment, filler and wetting agent along with it.

Typical example.—The coating compositions can be prepared simply by mixing the various ingredients. As a typical example of a preferred procedure for preparing the compositions, the wetting agent is added to the pigment at room temperature (between 60 and 70° F.), and the mixture is milled on a high-speed disperser mill while controlling the temperature of the mill to about room temperature. Alternatively, a Lightnin mixer can be used, e.g. where a predispersed pigment is included in the composition and less severe mixing is needed. After mixing on the mill, the clay and a portion of the water are added, preferably with the clay being added before the water. A solution or dispersion, e.g. latex, of the binder in water is then added and, if casein or the like is used, the pH is adjusted with ammonium hydroxide to provide a proper pH for the binder while agitating. Where a casein binder is used, it is preferred to pre-soak the casein in water for a short period of time to solubilize the casein before adding it to the composition. The rest of the water and any preservative or other additive are then added.

The prepared aqueous composition is then coated on a paper surface in an amount sufficient to give a layer of the desired thickness. The layer should be of sufficient thickness to provide pigment for transfer of a legible mark, and the upper limit of thickness will generally be limited by economics. A preferred coat weight is in the range of about 2.3 to about 3.5 lbs./3000 sq. ft.

The receptor surface **14** should be of a color or shade contrasting with that of the transfer coating so that a legible mark can be transferred. In the preferred form, the receptor surface **14** has a thin layer of wax coated thereon. The receptor surface preferably consists of a thin wax layer, and especially preferred is a water-white paraffin wax having a melting point of about 150–155° F. The wax is merely melted and spread by usual wax coating methods. The wax coat weight theoretically need be only molecular thickness, and the thickness should not be so great as to render the sheet incapable of transmitting writing or printing pressure.

The following examples of coating compositions are given by way of illustration of the invention and are not intended as limiting thereon.

Example I

10 gms. of Suco Peacock toner, a blue pigment, are mixed with 50 gms. of water in a Waring Blendor. 75 gms. of Huber 80 clay (kaolin) were added to form a slurry. A casein paste binder was prepared by adding 15 gms. of casein to 85 gms. of water. The binder was permitted to stand for about 15 to 20 minutes and was adjusted to a pH of 8.0 with ammonium hydroxide. 63 gms. of the casein paste were added to the water-clay-pigment slurry. 90 gms. of Pluronic L–62 (molecular weight of about 2000) were then added to the slurry and mixed in the blender until complete dispersion was attained. The pH of the mixture was adjusted to about 8 during mixing. The resulting composition was coated on a backing surface of a paper sheet and dried and was tested by typewriting on the front surface of the sheet with a second sheet of paper in facial contact with the coated backing surface. The transferred copy made on the second sheet of paper was a sharp blue image and had good smudge resistance.

Example II

10 parts by weight of Nycobrilliant carbon black, 5 parts of titanium dioxide and 90 parts of Pluronic L–62 were mixed on a ball mill for a five-minute grind period. 75 parts of Huber 80 clay and 60 parts of water were added to the mill and grinding was continued for 10 more minutes. 6 parts of a casein solution prepared as in Example I (containing 15% casein in distilled water) was prepared by soaking the casein in the distilled water for 45 minutes, agitating and adjusting the pH to 8.5 by addition of ammonium hydroxide, and the resulting casein solution was added to the ball mill and grinding was continued for an additional 5 minutes. 2 parts of water and 5 parts of titanium dioxide were then added and grinding was continued an additional 5 minutes. The pH of the resulting coating material was 7.5 and was again readjusted to 8.5 to 9.0 with ammonium hydroxide. The composition was then coated on a sheet of paper and dried and tested as in Example I and was found to have excellent smudge and release or transfer properties.

In dealing with highly surface-active wetting agents such as Pluronic L–62, some such agents have a low cloud point; and it is preferred to maintain the mixing and grinding temperatures, by temperature control, below a cloud point, about 85° F. in the case of Pluronic L–62. For example, during Example II, the mill was maintained at 56° F. by circulating cold water through the cooling jacket.

Where it is desired to use other additional agents, such agents can be added any time during the mixing. For example, the procedure of Example II was repeated and, after addition of the second portion of the titanium

dioxide, an insert of Dowicide A, a commercial preservative, in water was added to the composition to give a conecntration of Dowicide A of 0.2 percent by weight of the total composition.

Other runs like Example II, but varying the casein content from 3 to 10 weight percent based on total composition, were made. Based on such runs, it is especially preferred to use 3.5 to 4.5 weight percent casein.

Example III

The procedure of Example II was repeated except that the front surface of the second sheet was precoated with a layer of paraffin wax having a melting point of 150–155° F. with a coat weight of 2½ lbs./3000 sq. ft. The results showed excellent transfer and non-smudge properties of the transfer composition.

Example IV

Using the procedure of Example I, a coating composition was prepared from the amounts of materials listed below:

Ingredient:	Grams
Pigment (Aqua Black K, an aqueous dispersion of carbon black)	10
Titanium dioxide	10
Pluronic L–62	90
Huber 80 clay	75
H_2O	50
Polyvinylalcohol (Airco 325 grade) (17% solution in water)	65

Example V

Using the procedure of Example II, a coating composition was prepared from the amount of ingredients listed below for each of Examples V through X:

Ingredient:	Grams
Pigment (Nycobrilliant black)	10
Titanium dioxide	10
Pluronic L–62	45
Huber 80 clay	75
Casein (15% in water)	63
H_2O	96

Example VI

Ingredient:	Grams
Pigment (Nycobrilliant black)	10
Titanium dioxide	10
Pluronic L–62	60
China clay	75
Casein (15% in water)	63
H_2O	81

Example VII

Ingredient:	Grams
Pigment (Nycobrilliant black)	4
Titanium dioxide	10
Pluronic L–62	35
Huber 80 clay	50
Casein (15% in water)	40
H_2O	60

Example VIII

Ingredient:	Grams
Pigment (Nycobrilliant black)	10
Zinc oxide	10
Pluronic L–62	105
Huber 80 clay	75
Casein (15% in water)	63
H_2O	36

Example IX

Ingredient:	Grams
Pigment (Nycobrilliant black)	10
Titanium dioxide	10
Pluronic L–62	120
China clay	75
Casein (15% in water)	63
H_2O	21

Example X

Ingredient:	Grams
Pigment (Nycobrilliant black)	10
Titanium dioxide	10
Pluronic L–62	141
Huber 80 clay	75
Casein (15% in water)	63

The compositions of Examples IV–X were coated on paper at a coat weight of about 3 lb./3,000 sq. ft. and were tested for transfer and non-smudge properties using wax coated receptor surfaces as in Example III. Transferability in each instance was good or excellent and non-smudge characteristics were usually good, especially at low and medium levels of Pluronic content.

Additional examples were prepared by the procedure of Example II to screen other surface-active wetting agents by substituting the wetting agents in approximately the ratios of the following general formulation.

Ingredient:	Parts by weight
Pigment (Nycobrilliant black)	10
Titanium dioxide	10
Huber 80 clay	75
Wetting agent	60
Casein (15% solution in water)	65
Additional water	85

The wetting agents used for each example are identified as follows:

Example:	Wetting agent
XI	Pluronic L–62 (ethyleneoxide-polypropylene glycol).
XII	Pluronic L–64 (ethyleneoxide-polypropylene glycol).
XIII	Pluronic L–44 (ethyleneoxide-polypropylene glycol).
XIV	Santomerse 1 (alkyl aryl sulfonate).
XV	Anionic 4 (sodium tetradecyl sulfate).
XVI	Triton X100 (octyl phenol reacted with 9–10 mols ethylene oxide).
XVII	Tergitol 35 (nonyl phenol reacted with about 15 mols ethylene oxide).
XVIII	Tergitol 40 (nonyl phenol reacted with about 20 mols ethylene oxide).
XIX	Ethomid 0/15 (ethyleneoxide-oleyl amide).
XX	Tween 80 (polyoxyethylene sorbitan monooleate).
XXI	Surfynol TG (ditertiary acetylenic glycol).
XXII	Surfynol PC (ditertiary acetylenic glycol).
XXIII	Hercules AD160 (ethyleneoxide adducts of hydroabietyl alcohol).
XXIV	Duomeen TDO (dioleate salt of tallow diamine).
XXV	Hercules AF100 (ethyleneoxide adducts of alkylated phenol).
XXVI	Hercules AR150 (ethyleneoxide adducts of pale wood rosin).

When tested using the wax coated receptor surface as in Example III, Examples XI–XX gave excellent transfer and good non-smudge results. Each of Examples XXI–XXVI gave good transfer but in some instances the transferred image tended to smudge. However, attempts were not made to find the optimum amounts for the wetting agents of Examples XII–XXVI. The smudge problem can be lessened or overcome by varying the amount of wetting agent and/or binder as discussed above.

Still additional runs were made using the Pluronic L–62 wetting agent in the general formulation given above but substituting various other water soluble or latex-type binders. Such binders as polyvinylalcohol, polyvinylether-maleic anhydride, butadiene-styrene latex (Ucar), etheri-

fied polmeric carbohydrate (Ceron) and a protein of the binder of the glue type obtainable from Swift and Company, gave good results with respect to transferability and non-smudge of the transferred image. Although amounts of from about ¼ to about 10% of some of these binders were tested, and all gave some indication of transfer, the best transfer was obtained below 5% binder. The binders were included as solutions or latexes having from about 10 to about 40% binder in water. One or two percent by weight of the binder is usually considered adequate. Other than in the case of casein, experiments have not been directed to determining the optimum amount of binder.

It is apparent from the foregoing description of various embodiments that this invention provides a transfer composition which is capable of coating on the reverse side of a sheet of paper and is capable of transferring marks made from the front surface of the paper to another surface backing the transfer coating. The composition provides excellent transfer of a clear image with no appreciable smudging under normal conditions of use. Sheets coated with the composition can be manifolded to enable production of up to 20 or more copies with good transfer even on the last copy. The composition includes a binder and a surface-active wetting agent, which are preferably present in proper amounts or proportions for providing the excellent transferability and good non-smudge characteristics. Although examples of various compositions containing binders and surface-active wetting agents have been given, it is not the intent to be bound by the specific examples or their specific proportions since it is apparent that other binders and surface-active wetting agents, even in other proportions, are also operable. Upon selection of a binder and wetting agent for use in the composition the optimum amounts or proportions can readily be determined in the manner exemplified hereinabove.

All percents given herein are percents by weight and all parts are parts by weight unless otherwise indicated.

I claim:

1. A transfer sheet comprising a pressure transmitting sheet having a mark receiving surface and a backing surface, and a transfer coating on said backing surface, said coating consisting essentially of 2 to 10 parts by weight of a water-soluble adhesive binder selected from the class consisting of protein binders, polymeric carbohydrates and water soluble synthetic polymeric resins, 5 to 30 parts by weight of a normally liquid water soluble, organic, highly surface-active wetting agent which boils above the boiling point of water and which is selected from the group consisting of sulfonate, sulfate, ditertiary acetylenic glycol, a fatty salt of N-fatty alkylene diamine, and non-ionic surface-active condensation products of alkylene oxide with a hydrophobic base, a pigment, and a filler of finely divided clay in an amount bodying said composition to transfer consistency.

2. The transfer sheet of claim **1** wherein said adhesive binder consists essentially of casein.

3. The transfer sheet of claim **1** wherein said wetting agent contains plural alkylene oxide groups.

4. The transfer sheet of claim **3** wherein the wetting agent is ethyleneoxide-polypropylene glycol.

5. The composition of claim **1** wherein said wetting agent is a non-ionic surface-active condensation product of ethyleneoxide with a hydrophobic base.

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MURRAY KATZ, *Primary Examiner.*

U.S. Cl. X.R.

106—24, 26; 117—36.3; 260—29.1

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,446,647 May 27, 1969

John S. Rizner

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, line 4, "Varco Incorporated" should read -- Uarco Incorporated --.

Signed and sealed this 21st day of October 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents