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TRANSFER PRINT RECEIVING PAPER AND METHOD OF PRODUCING SAME

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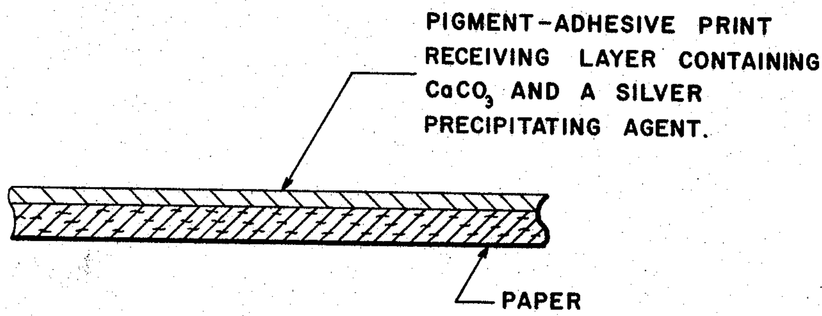

FIG. 1

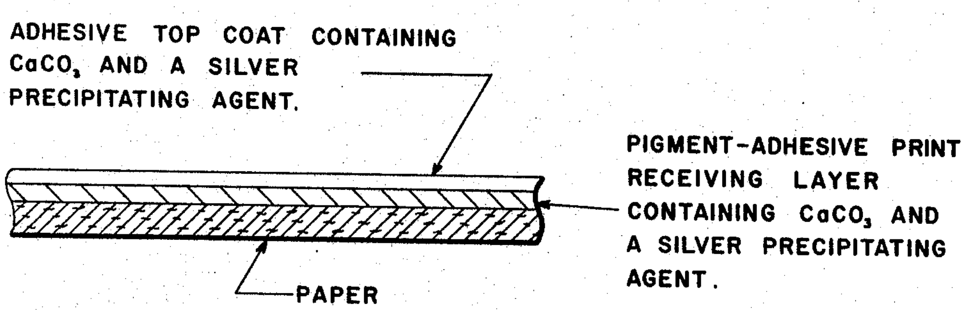

FIG. 2

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TRANSFER PRINT RECEIVING PAPER AND METHOD OF PRODUCING SAME

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This invention relates to improvements in the production of print receiving sheets for use in the diffusion transfer process, and to the products produced thereby.

In the diffusion transfer process a light sensitive silver halide coated "negative" is exposed to a light image. Subsequent development of this negative with a developer containing a silver halide solvent immobilizes the silver in the light struck areas of the negative, at the same time dissolving the silver halide in the non-light struck areas, and subsequently transferring at least a portion of the dissolved silver halide to a print receiving sheet brought in contact with the developing negative where it forms a positive image by reaction with materials present in the print receiving sheet. The print receiving sheet is then separated from the negative and allowed to dry.

The print receiving sheets heretofore used in this process have been laboriously prepared using methods and materials common to the photographic art. These prior art methods and materials, particularly the coating compositions are not adaptable to high speed low cost production.

Unexpectedly, I have found that a commercially satisfactory print receiving sheet can be produced in a manner and at speeds similar to that used for producing coated printing papers. Furthermore, I have found that the addition of a small amount of silver precipitating agent to a pigment-adhesive coating composition such as is used for producing coated printing papers produces a coating composition which upon drying is a satisfactory print receiving layer for use in the diffusion transfer process. Such coatings can be easily adapted for application on or off the papermachine.

Accordingly, an object is to produce a satisfactory print receiving sheet for use in the diffusion transfer process using inexpensive materials.

Another object is to provide a coating composition which can be coated on a base using commercial paper coating equipment to form a print receiving layer for the diffusion transfer sheet.

A further object is to provide a process especially adaptable to high speed production of a print receiving sheet for the diffusion transfer process.

FIG. 1 is a diagrammatic cross sectional view of a diffusion transfer print receiving sheet produced according to this invention.

FIG. 2 is a diagrammatic cross sectional view of a preferred form of diffusion transfer print receiving sheet produced according to this invention.

The rawstock of the instant invention can be any well-formed well-bonded coating paper rawstock which has been sufficiently beater and/or tubsized to minimize penetration of the alkaline developer during print development. Penetration of the rawstock by some of the alkaline developers leads to yellowing of the sheet on aging. Satisfactory sizing can be obtained with conventional paper sizing materials, for example, rosin-alum, stearates, ketene dimers, or wax sizes applied in the beater or at the tub. Tub sizing with water wettable but difficultly soluble film formers, such as starches or polyvinyl alcohols, in addition to the beater sizing assists in preventing developer penetration as well as improve the surface bonding of the rawstock. The improved surface bonding reduces rawstock "pick" during separation of the print re-

ceiving sheet from the light sensitive negative. Pick is also reduced by including up to about 3% starch in the beater and keeping the filler content at a low level, preferably below 5% of the beater furnish, or by the use of a wet strength resin, such as up to about 3% melamine-aldehyde resin, in the beater.

The print receiving layer is preferably formed by roll coating the rawstock surface with in the order of 6 pounds of solids per 3300 square feet of a pigment-adhesive coating composition containing a silver precipitating agent. Such a coating may easily be applied directly on the papermachine at speeds in excess of 600 feet per minute. Other methods of applying this coating, such as reverse roll, air knife, and trailing blade, may be used.

The print receiving layer may be applied to one or both sides of the rawstock as desired. If coated on both sides, either or both sides may be to develop the positive image. This ability to print on either side provides a definite advantage over the prior art print receiving sheets which because of the expensive materials used had a print receptive coating only on one side of the sheet. Another advantage of coating both sides is that the print receiving layer inhibits the penetration of the developer into the rawstock during development and thus helps to prevent yellowing of the rawstock on aging. Papers coated on only one side with the print receiving layer tend to show some yellowing on aging.

In formulating the pigment-adhesive composition for the print receiving layer, the preferred ratio of pigment to adhesive is in the range of 65 to 75% pigment and 25 to 35% adhesive, although these limits can be extended, for example, to 50 to 85% pigment and 15 to 50% adhesive depending on the method of coating.

Commonly used paper coating adhesives, such as starch, starch derivatives, starch-latex mixtures, and starch-polyvinyl alcohol mixtures can be used as the adhesive portion of the coating composition. Paper coating pigments such as clays, calcium carbonate, titanium dioxide, zinc oxide, aluminum oxide, and satin white can be used as the pigment portion of the coating composition. A mixture of these pigments may be used to arrive at the desired rheological properties of the coating composition and appearance of the finished sheet. The inclusion of 5% or more of calcium carbonate in the print receiving layer insures the formation of a black image on development. Apparently the calcium carbonate agglomerates the silver precipitating agent and thus gives a megascopically intense black image. The pigment should be sufficiently dispersed in the coating composition to insure effective distribution in the adhesive portion and to prevent graininess in the developed black image.

In the preferred form of the invention a thin top coat of starch, starch derivatives, polyvinyl alcohol or mixtures thereof containing a silver precipitating agent and from 1 to 30% calcium carbonate is applied over the print receiving layer. The top coating composition is preferably applied at about 1 pound of dry solids per 3300 square feet using a trailing blade coater, although other methods of coating can be used. Speeds in excess of 1000 feet per minute can be obtained if 5 to 15% calcium carbonate is present in the coating composition. The top coat blisters at these speeds if the calcium carbonate is omitted. In addition to materially intensifying the developed black image, the top coating is formulated to control "sliminess" of the developed surface and to minimize rawstock pick. Any coating pattern in the print receiving layer is minimized by top coating. Optical brighteners may be added if desired.

Any suitable silver precipitating agent, particularly the metal sulfides and selenides, such as the sulfides of zinc, cadmium, chromium, copper, cobalt, nickel, lead and silver and the selenides of zinc, nickel, and copper, can be used in either the print receiving coating or the top coating. Copper sulfide, silver sulfide and zinc sulfide are preferred for the coating compositions of this invention. The silver precipitating agents are formed "in situ" in the coating compositions by adding a water solution of a water soluble metal salt followed by a water solution of an alkali sulfide, such as sodium sulfide, mixing the coating composition thoroughly after each addition. For best results, the metal salt is added in considerable excess of the stoichiometric amount necessary to react with the sulfide present. A stoichiometric ratio in the order of 3 equivalents of metal ion to 1 equivalent of sulfide ion produces a black image. Lower ratios of metal ion to sulfide ion frequently produces a brownish image.

Without limiting this invention the following examples are given by way of illustration.

Example 1

A paper having a basis weight of 46 pounds per 3300 square feet was formed on a papermachine using a fiber furnish of approximately 40% softwood kraft and 60% hardwood kraft to which 50 pounds of titanium dioxide, 145 pounds of beater starch, 56 pounds of rosin size and 7.15 pounds of papermakers alum were added per 3300 pounds of fiber furnish. This sized rawstock was machine calendered and then roll coated both sides on the papermachine at a speed in the order of 600 feet per minute with a coating of the following composition:

	Parts by weight of solids
Coating clay	50
Calcium carbonate	10
Titanium dioxide	10
Enzyme converted starch	23
Butadiene-styrene latex	7
Calcium stearate	1
Sodium hexametaphosphate	1.5
Dicyandiamide	4.5
$CuSO_4 \cdot 5H_2O$	0.04
$Na_2S \cdot 9H_2O$	0.015

The coating composition was prepared by kneading together all of the pigments with calcium stearate, sodium hexametaphosphate, and dicyandiamide. A defoamer, such as Vegetol, may be added if desired. The copper sulfate was dissolved in water and added with the previously prepared 25% starch dispersion to the dry materials in the kneader. After kneading to a thick paste, the latex was added, and finally the sodium sulfide was dissolved in water buffered to a pH of 8.5 with sodium carbonate and added with thorough mixing to the coating composition. Dried coat weights of about 7 pounds per 3300 square feet were applied to both felt and wire sides of the rawstock using the above coating composition at approximately 56% solids.

After machine calendering, the pre-coated paper was top coated on each side with about 1 pound of solids per 3300 square feet of a coating having the following composition. The coating was applied by means of a blade coater at about 1000 feet per minute.

	Parts by weight of solids
Polyvinyl alcohol	25
Ethoxylated starch	55
Calcium carbonate	10
Optical brightener	10
Soda ash	1.6
$AgNO_3$	0.1
$Na_2S \cdot 9H_2O$	0.02

The coating composition was prepared by dissolving the soda ash in water and slurrying the calcium carbonate in this solution followed by sifting in the polyvinyl alcohol and starch and wetting out this mixture for a period of about 30 minutes. This mixture was then cooked at 190° F. for about 40 minutes at about 14% solids. After cooling the mixture to 100° F., the optical brightener followed first by a water solution of the silver nitrate and then by a water solution of sodium sulfide were added, mixing thoroughly after each addition.

The print receiving sheet prepared as above was used as a positive against a standard light sensitive negative and developed using an alkaline hydroquinone type developer. A well defined megascopically intense black image was produced using either side of the print receiving sheet. The sheet peeled from the negative even after 30 second contact without observable picking of the rawstock, and the sheet did not yellow on aging.

Example 2

A rawstock produced as in Example 1 was coated on each side with about 6 pounds of solids per 3300 square feet of a coating having the following composition. The coating was applied by roll coating on the papermachine at about 600 feet per minute.

	Parts by weight of dry solids
Coating clay	57
Calcium carbonate	10
Titanium dioxide	10
Enzyme converted starch	12
Polyvinyl alcohol	4
Butadiene-styrene latex	7
Calcium stearate	1
Dicyandiamide	4.5
Sodium hexametaphosphate	0.5
$CuSO_4 \cdot 5H_2O$	0.04
$Na_2S \cdot 9H_2O$	0.015

This coating composition was prepared as in Example 1 except that the polyvinyl alcohol was cooked separately at 14% solids and added to the knead with the starch.

The print receiving sheet prepared as above was tested as in Example 1. A black image was formed on development with an alkaline hydroquinone developer, the sheet peeled easily from the negative, and no yellowing of the sheet was observed on aging.

Example 3

Example 2 was repeated replacing the 0.04 part

$CuSO_4 \cdot 5H_2O$

with 0.04 part of $ZnSO_4 \cdot 7H_2O$. On testing the resultant sheet, a black image was formed on development with an alkaline hydroquinone developer, the sheet peeled easily from the negative, and no yellowing of the sheet was observed on aging.

The products and processes herein described are for purposes of illustration only, and it is understood that the invention includes all modifications and equivalents which fall within the scope of the invention which is defined by the appended claims.

What is claimed is:

1. A print receiving sheet comprising a sized paper rawstock having two sides, and print receiving layers superimposed on said sides of said paper rawstock, said print receiving layers comprising 57 parts by weight of coating clay, 10 parts by weight of calcium carbonate, 10 parts by weight of titanium dioxide, 12 parts by weight of starch, 4 parts by weight of polyvinyl alcohol, 7 parts by weight of butadiene-styrene latex, 0.04 part by weight of copper sulfate and 0.015 part by weight of sodium sulfide.

2. A print receiving sheet comprising a sized paper rawstock having two sides, print receiving layers superimposed on said sides of said paper rawstock, and top coats superimposed on said print receiving layers, said print receiving layers comprising 50 parts by weight of coating clay, 10 parts by weight of calcium carbonate, 10 parts by weight of titanium dioxide, 23 parts by weight of starch, 7 parts by weight of butadiene-styrene latex, 0.04 part by weight of copper sulfate, and 0.015 part by weight of sodium sulfide, said top coats consisting essentially of 10 parts by weight of calcium carbonate, 10 parts by weight of optical brightener, 25 parts by weight of polyvinyl alcohol, 55 parts by weight of ethoxylated starch, 1.6 parts by weight of soda ash, 0.1 part by weight of silver nitrate and 0.02 part by weight of sodium sulfide.

3. A print receiving sheet comprising a paper rawstock and a print receiving layer superimposed on said paper rawstock, said print receiving layer comprising 15 to 50% adhesive, 50% to 85% pigment, said pigment comprising at least 5% by weight of calcium carbonate based on the total weight of said print receiving layer, and a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides.

4. The product of claim **3** in which the silver precipitating agent is copper sulfide.

5. The product of claim **3** in which the silver precipitating agent is silver sulfide.

6. The product of claim **3** in which the silver precipitating agent is zinc sulfide.

7. A print receiving sheet comprising a paper rawstock, a print receiving layer superimposed on said paper rawstock and a top coat superimposed on said print receiving layer, said print receiving layer comprising 15 to 50% adhesive, 50 to 85% pigment, said pigment comprising at least 5% by weight of calcium carbonate based on the total weight of said print receiving layer, and a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides, said top coat comprising 1 to 30% calcium carbonate, 70 to 99% adhesive and a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides.

8. In the preparation of a coating composition for production of a print receiving sheet for the diffusion transfer process, the step of adding a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides to said coating composition, said coating composition comprising 15 to 50% adhesive solids and 50 to 85% pigment solids, said pigment comprising at least 5% by weight of calcium carbonate based on the total solids of said pigment-adhesive coating composition.

9. The process of claim **8** in which the silver precipitating agent is formed in situ in the pigment-adhesive coating composition.

10. The process of claim **9** in which the silver precipitating agent is formed by the steps of adding in sequence a water solution of a metal salt and a water solution of an alkali sulfide to said pigment-adhesive coating composition during preparation of said coating composition, said metal salt and said alkali sulfide being present in said coating composition in a stoichiometric ratio of about 3 equivalents of metal salt to 1 equivalent of alkali sulfide.

11. A process for preparing a print receiving sheet for the diffusion transfer process comprising the steps of applying a pigment-adhesive coating composition to at least one side of a paper rawstock and drying said pigment-adhesive coating composition to form a print receiving layer, said coating composition comprising 15 to 50% adhesive solids, 50 to 85% pigment solids, said pigment comprising at least 5% by weight of calcium carbonate based on the total solids of said pigment-adhesive coating composition, and a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides.

12. A process for preparing a print receiving sheet for the diffusion transfer process comprising the steps of applying a pigment-adhesive coating composition to at least one side of a paper rawstock, drying said pigment-adhesive coating composition to form a print receiving layer, said coating composition comprising 15 to 50% adhesive solids and 50 to 85% pigment solids, said pigment comprising at least 5% by weight of calcium carbonate based on the total solids of said pigment-adhesive coating composition, and a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides, applying a second coating composition over said print receiving layer and drying said coating composition to form a top coat, said second coating composition comprising 1 to 30% calcium carbonate solids, 70 to 99% adhesive solids, and a silver precipitating agent selected from the group consisting of metal sulfides and metal selenides.

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