Feb. 26, 1963 J. C. CORTEZ 3,079,270

AUTO COPY PAPER AND METHODS OF MAKING THE SAME

Filed March 6, 1959 3 Sheets-Sheet 1

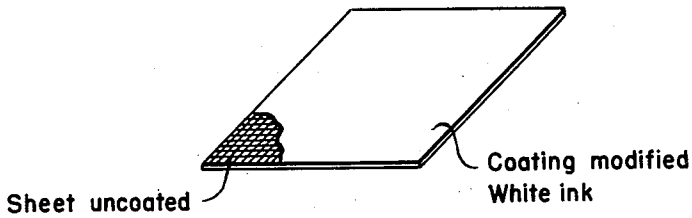


FIG.1

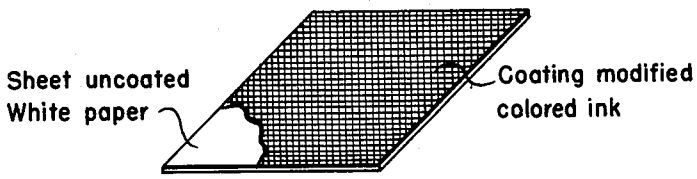


FIG.2

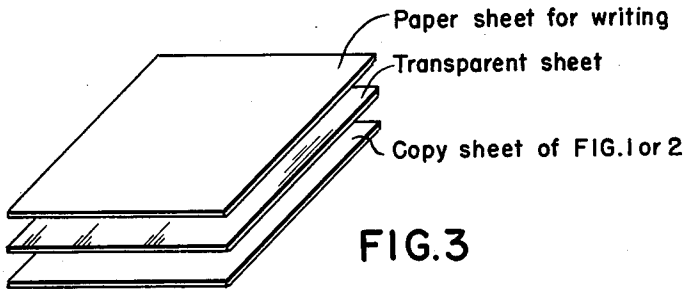


FIG.3

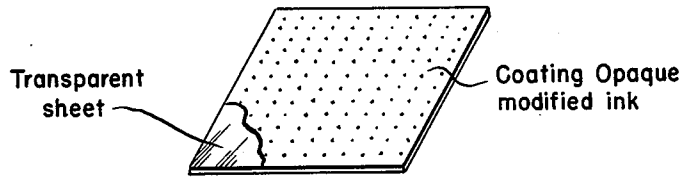


FIG.4

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AUTO COPY PAPER AND METHODS OF MAKING THE SAME

Filed March 6, 1959 3 Sheets-Sheet 2

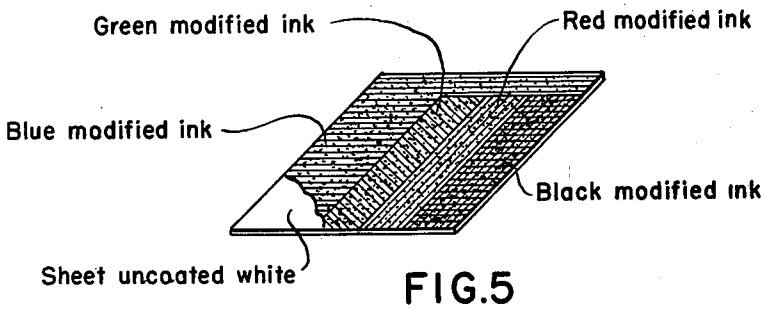


FIG.5

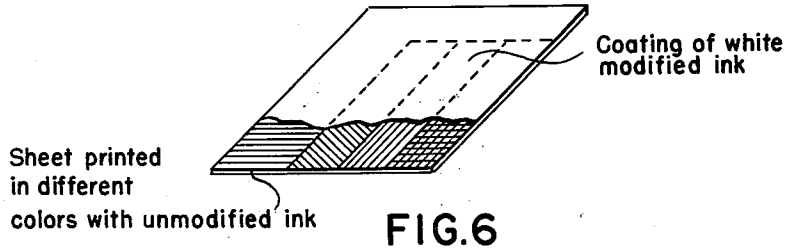


FIG.6

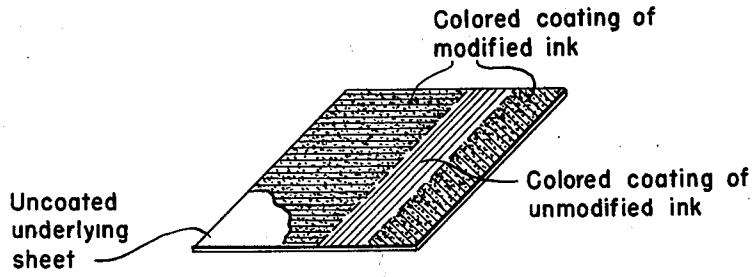


FIG.7

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Feb. 26, 1963 J. C. CORTEZ 3,079,270

AUTO COPY PAPER AND METHODS OF MAKING THE SAME

Filed March 6, 1959 3 Sheets-Sheet 3

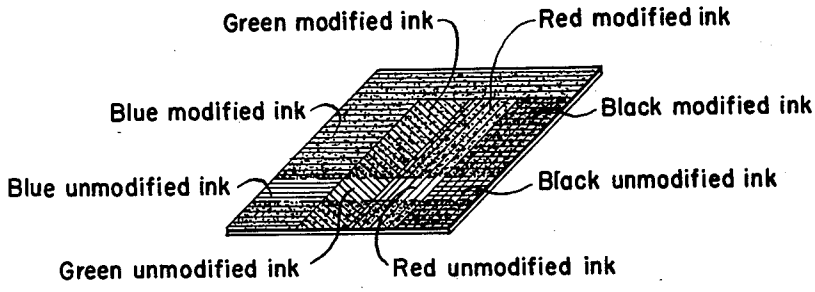


FIG.8

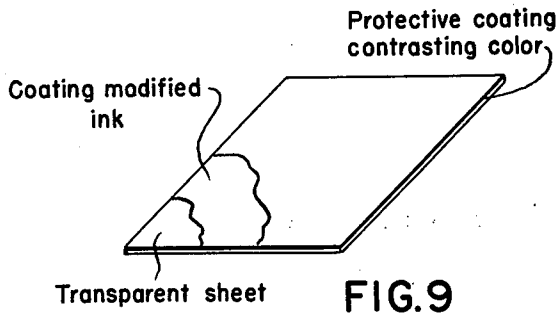


FIG.9

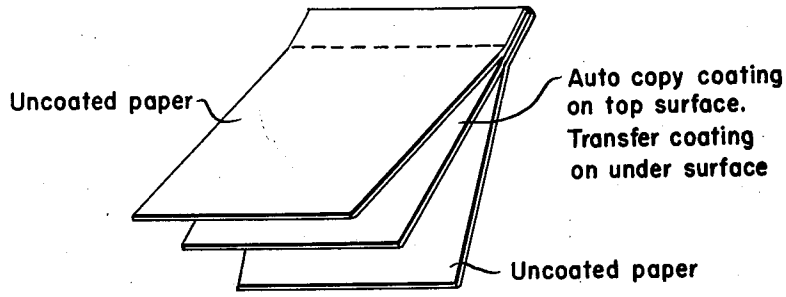


FIG.10

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United States Patent Office 3,079,270 Patented Feb. 26, 1963

3,079,270
AUTO COPY PAPER AND METHODS OF MAKING THE SAME

Jose C. Cortez, New York, N.Y., assignor to Lamford Paper International Ltd., Montreal, Quebec, Canada, a Canadian company

Filed Mar. 6, 1959, Ser. No. 797,721
17 Claims. (Cl. 117—36.7)

This application relates to improvements in copy papers and methods of making the same, and is a continuation in part of my pending applications Ser. No. 242,841, filed August 21, 1951, and Serial No. 340,141, filed March 3, 1953, both now abandoned. Copy papers of the character to which this invention relates are termed "auto" copy papers and are employed for making a number of copies of an inscribed or typewritten manuscript simultaneously without the use of a carbon or like sheet interleaved with the several sheets upon which the duplicate records are made.

For many years a great deal of effort has been expended in the development of auto copy papers in an attempt to do away with the use of carbon copy paper which has a number of well recognized drawbacks which need not be recited here. However, notwithstanding this very considerable effort heretofore expended in an attempt to produce a satisfactory copy paper, the great majority of duplicate copies that are produced simultaneously with the writing of the original are carbon copies made with interleaved sheets upon which the copies are made or by a layer of carbon on the backs of the overlying sheets.

Of the many types of auto copy papers heretofore proposed the most successful consists of a sheet of colored paper having a surface coating of translucent wax or similar material which is rendered transparent by the compression resulting from the typewriter key, or by the pressure of a pen or stylus, to thereby make the underlying colored surface of the paper visible in the areas corresponding to the letters printed or marked on the uppermost sheet. Wax sheets are, however, open to a number of objections. The coatings heretofore used have low melting points and tend to blur and become opaque in the area of the markings when subjected to temperatures but little above the ordinary room temperature. The compositions heretofore used are damaged by water. Although not water-soluble in the usual sense, they are water-absorbent to such an extent that the record is liable to be destroyed if the sheets are subjected to undue dampness. Sheets with coatings such as heretofore used are considerably thicker than the ordinary paper used for duplicate copies, thereby reducing the number of copies that may be made. In fact, the commercial wax type auto copy sheets now available are thicker than the combined carbton and copy sheet which would otherwise be used, and are also stiffer and less capable of transmitting pressure through a limited area to an underlying sheet of like character, with the result that the number of legible copies that may be produced at a single writing is very limited.

A further defect in the copy papers of the prior art is that the coating of the sheets with the composition heretofore used can be carried out only on slow speed machines as compared, for example, with a high speed printing press, whereby the cost of the sheet is greatly increased over that of an ordinary printed sheet such as used for making commercial forms of the type most generally employed for multiple copies.

The object of the present invention is to provide auto copy paper which is in appearance and observable physical properties indistinguishable from ordinary coated paper of grades commonly used for making writing paper,

sales slips and the like, and which when used in an ordinary typewriter or tabulating machine will produce copies comparable to those produced by ordinary carbon paper. Coated printing papers are produced by applying to the surface of the paper sheet a coating consisting essentially of pigment such as calcium carbonate and an adhesive such as casein, the coating being applied either in a non-aqueous solvent by a printing operation or in aqueous suspension by a paper coating operation. These coatings when applied to the paper sheet form a continuous opaque film or layer adhering to the face of the paper sheet and providing a smooth surface for receiving the printed or typewritten legend.

In carrying out my invention I employ standard coating compositions containing sufficient pigment to form opaque coatings on the face of the paper and by the addition of substances which I have hereinafter designated as surface-active agents, I modify the characteristics of the coating in such manner that under the impact of a typewriter key or the pressure of a stylus the continuity and opacity of the coating are destroyed in the area impacted so as to reveal the surface of the underlying paper sheet. The underlying paper sheet may be dyed or its surface may be otherwise coated with a color contrasting with that of the pigmented coating so that in the impacted areas the surface of the underlying web will appear in a color contrasting with that of the surrounding coated surface. The modification of the pigmented coating by my invention does not significantly alter the appearance, flexibility, heat resistance, etc., of the coated sheet and my improved auto-copy paper may be used and handled in precisely the same manner as coated paper having conventional coatings which have not been modified by the addition of the so-called surface-active agent. Otherwise stated, the coating is a firm dye pigment coating of good ink receptivity, is not tacky and does not smear.

Suitable coating materials having the characteristics above set forth may be readily produced in the form of high speed printing inks by adding to such inks a surface-active agent such as diethylene glycol monostearate, pentaerythritol tetrastearate, glyceryl monostearate and the like or mixtures thereof, the amount of such surface-active agent being approximately the same as the quantity of pigment in the ink. The quantity of surface-active agent required is not critical and the amount required for optimum results varies with the surface-active agents employed, the characteristics of the pigments used and also the viscosity of the ink, as well as the nature of the pigment-extenders, flattening agents, film-formers and the like which are used in printing inks to improve their printing qualities. Generally speaking, the greater the quantity of surface-active agents employed in proportion to the pigment content, the greater the number of copies that can be made with the same machine operating in the same manner. Apparently as the percentage of surface-active agent is decreased the greater the impact required to obtain the same results. If too much of the surface-active agent is used the adherence of the coating to the surface may be so reduced that the paper will not withstand the handling required in making the record and in its subsequent use.

Printer's ink in its broadest sense consists of pigment and a carrier in which the pigment is suspended, and a suitable coating material or "modified ink" for producing my improved auto copy paper by a printing operation may be produced by adding to the pigment suspension a surface-active agent having the characteristics of the compounds above referred to. Such coating materials are in effect modified inks and may be applied in the same manner and by the same apparatus as the unmodified inks.

For example, a suitable modified white ink may be prepared according to the following formula:

	Parts
Diethylene glycol monostearate (Kessler's)	60
Mangnesium carbonate USP light powder (Baker's)	60
Ethylene dichloride (Jefferson's)	500

The ingredients may be mixed together at room temperature and stirred in a high speed mixer until a suitable suspension of the pigment and surface-active agent in the carrier is obtained.

The following additional formulas have been found satisfactory for the production of modified inks of different colors for use in various types of printing processes:

	Parts
White 2:	
Diethylene glycol monostearate	60
Magnesium carbonate USP light	60
Low viscosity Parlon, 9 c.p.s	5
Santocel C, sub-micro silica	1
Ethylene dichloride	500
White 3:	
Diethylene glycol monopalmitate	60
Magnesium carbonate USP light	60
Low viscosity polyclo rubber Pliolite 1230	8
Ethyl alcohol anhydrous	100
Toluol pure	400
White 4:	
Pentaerythritol tetrastearate	60
Magnesium carbonate—USP light	60
Low viscosity polyclo rubber Pliolite 1230	8
Ethyl alcohol anhydrous	100
Toluol pure	400
Blue 5:	
Glyceryl monomyristate	60
Victoria blue toner dry	2
Peacock blue lake dry	58
Low viscosity polyclo rubber Pliolite 1230	8
Ethyl alcohol anhydrous	100
Toluol pure	400
Black 6:	
Diethylene glycol monostearate	60
Lamp black	60
Low viscosity Parlon 9 c.p.s	8
Santocel C, sub-micro silica	2
Ethyl alcohol anhydrous	100
Toluol pure	400
Red 7:	
Ethylene glycol monomyristate	60
Red toner phloxine, dry	30
Alumina trihydrate dry	30
Low viscosity Parlon 9 c.p.s	6
Santocel C, sub-micro silica	2
Ethyl alcohol anhydrous	100
Toluol pure	400

When more than one solvent is to be employed, it has been proven more practical to mix the solvents beforehand in order to make up one solvent out of the combination, thus for example, the 100 parts of ethyl alcohol anhydrous and the 400 parts of toluol pure, specified in Formula 5 above, are mixed together to produce one solvent representing an 80–20 toluol-ethyl alcohol solution. In like manner other solvent combinations can be made. With those facts in mind I prefer to place in the high speed shear mixer, about one-third of the solvent to which the corresponding portion of the flatting agent is added first; the resulting mixture is stirred for about five minutes at the end of which, while the mixer is in motion, the corresponding portion of the film-forming agent is added with continuous stirring for about five minutes more before the incorporation of the pigment into this mixture is to be made. The pigment is then added little by little while the mixer is in motion at high speed until a dough-like mass is formed that allows proper and efficient shearing action by the mixer. Whenever this dough-like mass becomes too thick or heavy to allow proper shearing action, then suitable quantities of the surface-active agent are added to promote proper wetting action which will permit the further addition of pigment until all of the required quantity of the pigment called for by the specific formula has been incorporated and an even dough-like mass has been formed that will allow uniform, efficient shearing action by the mixer. The shearing operation is continued for about a half hour at the end of which, the rest of the surface-active agent is to be added, little by little until the dough-like mass becomes of the consistency of heavy cream; another half hour of shearing is continued and then the rest of the solvent is added slowly. The resulting mixture is then filtered through fine gauze and allowed to stand for six hours or more before applying the same by either printing or coating operations.

Modified inks may be prepared for application by a particular high speed printing press by selecting an ink which is suitable for operation in the press as an unmodified ink and modifying the ink by the addition of an appropriate quantity of a surface-active agent of the character above referred to. Satisfactory results will not ordinarily be obtained by merely adding the surface-active agent to the already compounded ink, but suitable modified inks may be made by compounding the ingredients making up the unmodified ink with the addition of the required amount of the surface-active agent and following the compounding procedure described above. In so compounding the ink it may be desirable to vary the quantity of solvent used in order that the modified ink shall have the same fluidity and drying characteristics as the unmodified ink. It may also be desirable to modify to a certain extent the flattening agents, pigment extenders and other ingredients of the unmodified ink in order for the modified ink to have precisely the same physical properties as the unmodified ink, but ordinarily an adjustment of the solvent content of the ink and the addition of the surface-active agent are the only formula changes required to produce a modified ink which may be substituted for the unmodified ink in the operation of the press.

By eliminating the volatile solvents entirely suitable coating compositions in the solid rather than in the liquid state can be made with the same materials in suitable proportions, in the form of solid, low viscosity, high speed, modified thermo-fluid inks which dry or set by exposure to cold instead of heat, upon contacting a cool surface, suitable for application in a melted condition by high speed rotary presses or by high speed, three-roll precision coaters having fountains, platens, metal rollers and forms specially heated above the melting point of the inks, as commonly employed for printing with cold-set inks or for high speed coating with hot-melts.

These modified thermo-fluid, cold-set, high speed inks can be manufactured simply by first melting in a steam-jacketed mixing kettle, to a point of fluidity a small quantity of the surface-active agent to which the corresponding quantity of the film-forming agent is then added with continuous stirring until the hot mixture reaches the consistency of taffy, at which point, another more substantial quantity of the surface-active agent is then added little by little with continuous stirring until a completely homogenous mixture is thereby obtained. The corresponding quantity of the flatting agent is then added and incorporated into the mixture with vigorous, continuous stirring and then, the rest of the corresponding quantity of the surface-active agent is finally added, little by little, with continuous vigorous stirring until a completely homogenous mixture is thereby again obtained. The temperature of the resulting mixture is now to be maintained evenly at a point well above the melting point of the surface-active agent, say about 85 to 95 degrees centigrade, at which point, the corresponding quantity of the pigment is incorporated little by little with vigorous continuous stirring until a completely homogenous pigmented mixture is obtained.

During this stirring and mixing operation, the degree of dispersion of the pigment into the vehicle is tested several times by means of a strip of aluminum foil which is dipped into the hot mixture and cooling the same by contacting a cool surface, for example, by wrapping the inked foil around a glass filled with ice cubes and then examining the coating when cold for evenness of pigment distribution or aggregates as the case may be; continuous vigorous stirring is continued until a perfect, even colored pigmented film is obtained on the aluminum foil. At this point, the steam or heat is shut off and the resulting mixture cooled down by continuous stirring until it reaches near to the solidification point. The resulting compound when cold is a solid which is broken into suitable chips and the chips milled to the highest degree of fineness obtainable in order to attain the maximum degrees of dispersion of the pigment into the binding component. Such milling operations sometimes are more efficiently carried out by means of refrigerated mills such as the ones commonly employed for the milling of synthetic resins and the like. The resulting solid represents a thermo-fluid, cold set modified high speed ink ready for use as previously described. Inks of the type referred to above can be readily obtained from the following or like formulas:

Black 1:	Parts by weight
Ethylene glycol monomyristate	60
Ethylene glycol monolaureate	10
Carbon black	25
Pliolite 1230	5
Blue 2:	
Glyceryl monopalmitate	60
Glyceryl monococate	10
Peacock blue dry	25
Pliolite 1230	5
White 3:	
Diethylene glycol monostearate	60
Diethylene glycol monococate	10
Zince oxide French process	25
Low viscosity ethyl cellulose	5

The addition of relatively small quantities of suitable inert flatting agents such as Santocell C or Bentones 18 and 34, in the order of one-tenth to five tenths of one percent of the total weight of the ink, improve considerably all of the desirable physical properties of the thermo-fluid inks.

As previously stated, the compounds which I have at this time found to be the most suitable for producing satisfactory auto copy papers are water-insoluble, chemically inert, non-ionic surface-active agents. These compounds are the products of reactions between alcohols and ethers of the polyhydric type, synthetic polyoxyalkylene condensates and the fatty acids, either natural or synthetic, plain or modified by hydrogenation or oxygenation of varying carbon chain length, derived from oils, fats, waxes, resins, oleoresins, gums, rosin and combinations thereof. By reacting properly these materials innumerable variations of mono, di, tri, etal. esters, ester-ethers, partial esters and combinations thereof are obtained ranging from low freezing point oily liquids at minus 16 degrees centigrade to relatively high melting solids at 70 degrees centigrade and above.

The pigments included in the above examples are opaque pigments which are customarily employed in producing inks of good hiding power for ordinary printing operations. I may, however, by this procedure above described produce modified transparent inks such as employed in multi-color printing where one color is overlaid on another color to produce the desired color effect. So far as I am personally aware, all the pigments commonly employed in the manufacture of printing inks, both opaque and transparent, may be suitably modified by the procedure above described.

The modified inks or coating compositions in the area impacted by the typewriter key adhere to the back of the overlying sheet in some instances, while in other cases the coating in the impacted area does not leave the paper but the continuity and opacity of the coating is so altered that the surface of the underlying sheet is as fully revealed as in those instances where the pigment particles do adhere to the overlying sheet. While it is not definitely known just why this different effect takes place, it has been observed that when diethylene glycol monostearate is used as the surface-active agent as in Example 2 above, the back of the overlying sheet does not apparently pick up any of the coating composition from the impacted areas, while coating made with pentaerythritol tetrastearate will produce on the back of the overlying sheet a clear replica in reverse of the record made on the copy sheet.

This adherence of the coating composition to the back of the overlying sheet may be prevented by treating the surface of the sheet with a suitable mold-releasing agent such as an organo silicon polymer, in which case the detached coating composition can be detected in the form of fine particles on the surface of the sheet from which they can be removed by merely shaking the sheet.

Just why the substitution of pentaerythritol tetrastearate for diethylene glycol monostearate makes this difference in the behavior of the coatings is unknown, as the two coatings in appearance and observable physical properties are the same.

The foregoing examples are for the most part modified inks for use in high speed printing presses as the use of such presses for the application of the modified inks to the surface of the paper is desirable from the standpoint of economy of manufacture. However, as stated above, my invention is applicable to inks adapted primarily for use in other types of printing apparatus. For example, presses of the so-called "silk screen" type may be successfully employed for the manufacture of auto copy paper in accordance with my invention. For such purpose an unmodified ink of the character employed in such presses may be "modified" by the addition of a suitable amount of an appropriate surface-active agent. As an example of a white ink for use in silk screen presses the following formula has been found satisfactory:

	Parts
Diethylene glycol monostearate	90
Magnesium carbonate	60
Crystal clear silk screen base (Sherwin-Williams)	45
Transparent silk screen base (Sherwin-Williams)	15
Naphtha	120

Ordinary printing inks consisting primarily of opaque pigment suspended in a vehicle of an oleaginous nature such, for example, as linseed oil, may also be modified by the addition of an appropriate quantity of a surface-active agent such as diethylene glycol monostearate in the order of one pound of surface-active agent to each pound of pigment (dry basis).

Just what happens to the pigment particles in the impacted area when sheets coated in the manner above described are used as copy sheets in a typewriter is not fully known. The coating before the sheet is used is a thin continuous opaque layer of oriented pigment particles adhering to the surface of the underlying sheet and to some extent filling the spaces between the surface fibers of the sheet so that the surface of the coating is smoother than the surface of the paper web. By the impact of the typewriter keys the continuity and opacity of the pigment layer are altered, for the surface of the underlying sheet is plainly visible in the areas impacted by the keys and the edges of characters are as clearly defined as the characters printed by the ink on the ribbon copy.

Sheets of uncoated paper dyed black having a thin coating of a white modified ink of the formula on page 13 above were used as copy sheets in a standard typewriter and then examined with reflected light under a microscope at 150× magnification. The dyed fibers

forming the surface of the underlying sheet were visible throughout the area of the characters examined and fine white particles were scattered over and apparently imbedded in the fibers. The crystal clear silk screen base of this formula is an alkyd resin and the transparent silk screen base is a combination of polymerized linseed oil and rosin oil.

Thin sheets of cellophane having thin opaque coatings of white modified ink of the formula in column 3 above were used in the same manner and similarly examined. The letters were clearly transparent and under the microscope fine white particles appeared to be scattered throughout the impacted areas.

Coating compositions wherein pigment is suspended in an aqueous vehicle such, for example, as the so-called water base inks used in the manufacture of wall paper, may similarly be modified and used in the manufacture of auto copy paper in accordance with my invention. Aqueous coating compositions have the advantage that they may be applied to the paper in the course of its manufacture by the ordinary paper coating apparatus now employed for the manufacture of ordinary coated paper.

As an example of a white ink for application by the usual paper coating machine the following formula is satisfactory:

	Parts
Diethylene glycol monostearate	90
Finely precipitated calcium carbonate	100
Casein dissolved in ammonia water	18
Water	150

Many of the water base inks and coating compositions now in use can be readily modified so as to have "auto-copy" properties.

A pigmented, water-base ink or coating composition for paper consists, in its simplest form, of a dissolved or colloidally dispersed solid, film-forming adhesive and a pigment which, when the water is removed, adheres to the fibrous paper base. The adhesive acts as a binder for the pigment particles so that these will not be "picked off" the sheet in the printing press. The pigment produces the desired color shade and makes the paper surface receptive to printing ink. The coating operation consists of laying down a continuous film of adhesive and pigment over the individual fibers and filling the hollows between them. The relative proportions of adhesive to pigment can be varied, but in general, the pigment comprises from 75 to 90% by weight of the dry ingredients and the adhesive comprises from 10 to 25%. The water content ranges from 70 to 30%, and conversely, the solids content of the coating or ink ranges from 30 to 70%. The adhesives used are: starch, gums, glue, casein, vegetable proteins, water-soluble cellulose, latex and synthetic resins. The pigments used are: clay, calcium carbonate, titanium dioxide, zinc oxide, satin white, gloss white, and similar pigments derived from calcium, barium, zinc, lead and the like.

In commercial practice, many coatings and inks are made with pigment blends, such as, clay-calcium carbonate-titanium dioxide, and the like, in order to combine the desirable properties of two or more pigments. Adhesives, on the other hand, are blended for inks but very seldom for coatings, with the exception of latex which is widely used in coatings with casein and in some cases with starch. In all cases, the major ingredients of the coating formula, are the adhesive and the pigment. However, commercial coatings and inks, always contain a number of other materials which are added as minor ingredients. These materials are not an essential part of the coating mixture or ink, but are added for special effects, mostly to facilitate the application of the ink or the coating mixture by means of high speed mechanical equipment. The materials commonly added as minor ingredients are: wax emulsions of carnauba, candelilla, ceresin, japan, paraffin and beeswax, glycerin, glycol, sorbitol, corn syrup, dextrin, yellow soap, castile soap, metallic soaps both soluble and insoluble, as sodium stearate, ammonium stearate, calcium stearate and the like, dispersing agents, in the order of sodium tetraphosphate, pyrophosphate, hexametaphosphate and ammonium caseinate and the like. Antifoaming agents in the order of octyl alcohol, fusel oil, pine oil, sulfonated oils and, finally, preservatives in the order of chlorinated phenols, beta-naphtol and the like. The coating or ink composition is usually prepared by dispersing the blend of pigments and the adhesive separately in water and then mixing the two together.

The following are specific examples of formulas for producing a water-base white pigmented ink for printing by rotogravure, and a water-base white pigmented coating composition for book paper for application by high speed roller coaters:

	Parts
Water-base white ink:	
Pigment slurry—	
Calcium carbonate	10
Zinc oxide	5
Titanium dioxide	10
Water	20
Adhesive vehicle solution—	
Glycerin	45
Soap	2
Yellow dextrin	5
Gum arabic	12
Water	100
White coating for book paper:	
Pigment slurry—	
Clay	100
Calcium carbonate	20
Sodium tetraphosphate	1
Water	60
Adhesive vehicle solution—	
Wax emulsion 12% solids	2
Soap	2
Turkey red oil	1
Enzyme converted starch	25
Water	100

A reduction of the film-foaming adhesives used in the formulas given above, that is to say, the yellow dextrin, the gum arabic and the enzyme converted starch respectively, plus the addition of a quantity of a solid, water-dispersible, non-ionic surface active agent, of melting point of 55 to 70 degrees centigrade and above, in the order of diethylene glycol monostearate, glyceryl monopalmitate, pentaerythritol tetrastearate and the like or combinations thereof, that will correspond on a pound per pound weight dry basis with that of the pigment content in the formulas, is the only change required to produce a modified, water-base pigmented white ink and a modified, water-base pigmented white coating composition which may be substituted for the unmodified ink and the coating composition in the operation of the rotopress and the roller coater, as the case may be, in order to produce auto copy papers.

Besides clay and the white pigments used in the formulas referred to above, there are many other pigments that may be used either alone or in blends which, in conjunction with surface-active agents, will produce suitable, modified, water-base pigmented inks and coating compositions for making auto copy papers, examples of these are: magnesium carbonate, magnesium oxide, magnesium silicate, barium carbonate, zinc sulphide, mica, talc, diatomaceous earth, silica, white low gelling bentonite, gloss white, satin white, silk white, blanc fixe and the like. In this connection, the following are typical specific examples of formulas for ready-modified, water-base pigmented coatings which have been found satisfactory for producing auto copy papers.

Example A

Pigment slurry:	Parts
Magnesium carbonate	100
Polyoxyethylene lauryl ether	0.1
Water	50
Binder vehicle solution:	
Diethylene glycol monostearate	90
Beeswax	10
Polyoxyethylene stearate	0.1
Water	450

Example B

Pigment slurry:	
Satin white	30
Water ground mica	10
Magnesium carbonate	60
Polyoxyethylene alkyl lauryl ether	0.1
Water	50
Binder vehicle solution:	
Polyethylene glycol stearate	90
Morpholine soap	5
Carnauba wax	5
Water-soluble cellulose	5
Water	450

Example C

Zinc sulphide	2
Blanc fixe	10
White bentonite	10
Talc	3
Magnesium carbonate	75
Polyoxyethylene lauryl ether	0.1
Water	50
Binder vehicle solution:	
Glyceryl monopalmitate	90
Polyoxyethylene stearate	10
Polyvinyl alcohol	10
Petroleum wax	10
Water	450

By virtue of the fact that the modified inks used in the manufacture of my improved auto-copy paper can be made in any color desired and can be printed on the paper or other sheet in any desired pattern, in different colors and in overlying layers with unmodified inks, many different types and forms of auto-copy paper may be made, some of which I have illustrated in the accompanying drawings.

FIG. 1 shows a sheet for making ordinary copies of typewritten material. The back of the sheet is preferably black or other dark color. On one surface of this sheet is a coating of modified white ink compounded, for example, in accordance with Formula No. 1 above and applied to the surface of the sheet 1 by a paper coating machine of the roll coater type. Instead of using dark paper and white modified ink, the sheet may be of ordinary white paper as shown in FIG. 2, with a coating of modified ink of any desired color, for example, blue, such as produced by Formula 5 above. Any desired combination of colors may be obtained by printing the sheet with unmodified ink of the color desired for the writing and then by a printing or coating operation, applying an overlying layer of modified ink of the color desired for the unprinted areas. If desired, a copy on a transparent sheet may be made with copy sheets such as shown in FIGS. 1 and 2 by using in the modified ink surface-active agents which effect the opacity of the ink in impacted areas intact as above described. Such a sheet is shown in FIG. 3.

For this purpose any thin transparent sheet material may be employed, such, for example, as cellophane, Pliofilm, cellulose acetate, tracing paper, glassine paper and the like. By interleaving the transparent sheet between the paper on which the written record is made and the first copy sheet there can be produced at one operation a typewritten "original," a transparent sheet having the record in opaque letters, and as many "copies" as desired. The transparent copy can be used for making photoprint copies of the document.

The surface of the transparent sheet may be treated to increase the adhesion of the detached coating composition by applying a weak solution of nitrocellulose lacquer or the like or may be slightly roughened by sanding. Unless the surface is exceptionally hard and smooth a satisfactory transparent record can be made without treatment of the surface of the sheet.

As the record on the transparent sheet is in reverse, sheets so made can be used with advantage for address labels and the like. For this purpose the surface of the transparent sheet adjacent the copy sheet may be treated with an adhesive which serves not only to enhance the adhesion of the detached coating to the surface of the sheet, but also to stick the sheet to the article to be labeled. The legend on the label is on the underside of the transparent label and is thus protected against moisture, abrasion, etc.

In FIG. 4 I have shown an opaque sheet having a record in transparent letters. This sheet may be formed by printing a coating of modified ink on a transparent sheet, such for example, as glassine paper or cellophane. When a sheet of this character is placed beneath the paper in a typewriter the modified ink will be detached in the areas impacted by the keys. Such a sheet will produce a positive blue print or photostat.

FIG. 5 shows a simple multicolor form particularly useful for tabulations in columns where it is desired to have each column appear in a distinctive color. Tabulated forms when so printed are much easier to read from the standpoint of speed and accuracy, and also as regards eye fatigue. As here shown each of the areas where figures forming the several columns are to be transcribed is printed with a different colored modified ink, all of which may be readily applied at a single operation by a suitable multicolor press or by a paper coating machine equipped with striping rolls.

In the form of sheet shown in FIG. 6 the figures forming the different columns appear in different colors and the different areas of the sheet also appear in different shades so that each separate area stands out distinctly whether or not figures are recorded therein. In this sheet the separate areas are printed in separate colors with unmodified inks and the whole sheet is then overlaid with a thick coating of white modified ink which does not have sufficient hiding power to completely mask the underlying colors. When a form of this kind is used the letters and figures appear in the bright colors of the underlying coatings of unmodified inks, the figures being surrounded by the unmodified white ink which, however, in each area is differently shaded by the underlying color.

In the sheet shown in FIG. 7 the paper is uncoated white paper with a coating formed in part of unmodified ink and in part of modified ink. A record will be made only in those areas where the modified ink is used. By using modified and unmodified inks of the same color it cannot be told from an inspection of the copy whether or not there was any writing on the portions of the ribbon copy sheet corresponding to the parts printed with unmodified inks. To better conceal the line of demarkation between the areas printed in the different kinds of ink the printing is preferably in the form of fine lines, as indicated.

In the sheet shown in FIG. 8 the multi-color arrangement of FIG. 5 is combined with the restricted copying feature of FIG. 7. In this sheet the different columns are printed in different colors as in FIG. 5, but different portions of the columns are printed in part with modified inks and in part with unmodified inks. To better mask the lines of demarkation between the areas printed with modified and unmodified inks the printing is preferably in horizontal finely spaced lines as above described.

In FIG. 9 I have illustrated an auto-copy paper which

is particularly suitable for use in modern business machines.

It is well known that the printing mechanism by which the record is made in modern high speed electronic business machines for recording in multiple copies, operates at a high rate of printing speed but with relatively low striking force at the type faces.

For example, a high speed electronic accounting machine for recording in multiple copies, such as IBM model No. 407, equipped with printing wheels mechanism and platen durometer 96–100, operates with a striking force at the type faces which is the equivalent of about one-third of the striking force at the type faces on an ordinary typewriter required to make five legible carbon copies on paper of the weight customarily employed for such purpose. Such machines, however, make 150 impressions per minute, and their usefulness would be greatly increased if more legible copies could be made.

Machines operating at the high speeds above mentioned are very destructive of ink ribbons. After a few hours continuous service the ribbons are so worn as to no longer make clean impressions. The frequent replacement of the ribbons is in itself costly and time consuming. Furthermore the lint from the frayed ribbons adheres to the type faces, necessitating frequent cleaning of the keys, which adds greatly to the expense and time lost.

Any of the above-described auto-copy papers may be used in ribbonless machines for a brief period of operation, but the impact of the keys on the coated surface of such paper results in particles of the coating adhering to the type face in the same manner as the lint of the frayed ink ribbons so that although the cost of ribbons and the shut-down time incidental to changing the ribbon is saved by the use of the above-described paper, there is still the necessity of frequently cleaning the type faces for the printing to continue to be clear and distinct.

With the sheet of FIG. 9 the coating is not on the side of the sheet exposed to the impact, but on the reverse side, and the sheet is made of material from which nothing is detached in the printing operation.

A thin sheet of glassine paper, cellophane or plain transparent tracing paper of suitable formation and tensile strength, is coated on one surface with a thin, even coat of a modified ink, for example, one of the formulas given in column 3.

I then print on the opaque layer of modified ink a backing layer of unmodified ink of a color different from the color of the modified ink so that when the opacity of the modified ink in the areas impacted by the type face is destroyed, the surface of the backing layer so exposed will make a clear and easily readable character against the surrounding areas where the layer of modified ink is unaffected. The backing layer forming the outer coating on the transparent sheet over the coating of the modified ink and which constitutes the back of the sheet after the sheet is printed or written upon should be thin and flexible and tenaciously inherent so as to serve as a protective shield against obliteration of the record by abrasion, dampness, heat and other external causes. For this purpose I have found that the incorporation in the unmodified ink of rubber-like materials which are themselves film-forming is advantageous, so that in effect the resulting sheet is in the nature of a sandwich with the layer of sensitive coating material between a transverse film on its top face and a backing film which will ordinarily be colored with a color different from that of the sensitive film. For example, this backing film may consist of Victoria blue ink base 15 parts; synthetic rubber Pliolite resin No. 5–5*b*, 5 parts; chlorinated diphenyl No. 5420, 3 parts, toluol 92 parts.

A blue ink of this composition may be applied to the paper by a high speed printing press in the same way as the layer of modified ink. The sheet so produced is blue on one side and white on the other side and with a transparent coating over the white layer, this transparent coating being in fact the sheet of glassine paper upon which the layers of modified and unmodified ink are applied in the manufacture of the sheet.

The backing film may, however, be transparent if it is desired to have a record wherein the characters are transparent to transmitted light. For this purpose the above composition may be used with the Victoria blue base omitted. As explained above, such sheets are useful for making direct photostatic copies or for producing optical projections of the sheet.

The composition forming the backing layer may be rendered opaque by the inclusion of pigments in the material as described, or the transparent layer may be rendered opaque by dusting the applied layer with pigments in powder or flake-like form, such as aluminum, magnesium, bronze and the like, to produce a continuous outer metallic surface in the order of one flake in thickness.

In addition to the pigment of a color different from that contained in the modified ink I may, if desired, apply a third layer of coating composition, either by way of dusting or otherwise, to the sheet, the third layer being the same color as the modified ink in order that the sheet present on both sides the same color, for example, white.

The coating on the paper of FIG. 9 may be applied as water base inks such as above described. For example, the transparent sheet may be coated with a thin, even coat of a modified, water-base white pigmented ink or coating composition of the above Example A, B, or C and then dried. The dried white coating is then overcoated with a thin film of any standard unmodified water-base ink or pigmented coating composition of a contrasting color, for example, black, dark blue or violet and the like. Such standard, unmodified, water-base inks and pigmented coating compositions as commonly employed in the manufacture of colored papers for fancy wrappers, decorations, wall papers and the like are perfectly suitable for this purpose. The following is an example of an unmodified, water-base black coating composition that may be used: black pulp, 35 parts, nigrosine dye, 0.1 part, talc, 1.90 parts, casein solution, 22 parts, beeswax emulsion 2 parts and water 22 parts. Other materials that may be used are: dyed or pigmented water-soluble adhesives properly plasticized, such as carboxymethyl cellulose, methyl cellulose, polyvinyl alcohol, converted starch, rubber latex, Saran and the like. In fact, almost any water-soluble, water-dispersible or emulsifiable, film-forming adhesive of combinations thereof which forms a film having sufficient strength to remain intact in unsupported areas coextensive with the impressed characters may be employed.

Also for the auto-copy sheet of FIG. 9 coatings of the prior art having auto-copy properties may be used. The coating is not exposed and consequently the properties of these prior art coatings which render them unsatisfactory for use on the exposed surface of a sheet do not prevent the use of these coatings in a sheet such as shown in FIG. 9.

In FIG. 10 I have shown a three-sheet leaflet for use in recording transactions in which only the middle sheet has auto-copy properties. This middle sheet is coated on both surfaces. The sheet is preferably of dark colored paper and has on its top face a coating of white modified ink of a formula which does not adhere to the back of the overlying sheet in the impacted areas. The coating on the back of the sheet is preferably of the same color as the sheet itself, and the coating is of a formula such that the pigment in the impacted areas will adhere to the sheet against which it is pressed and will therefore form a record on the third sheet which may be a printed form on paper or cardboard. This three sheet leaflet is suitable for most commercial transactions as it provides a sheet for the purchaser, a sheet for the seller, and a third sheet for accounting purposes.

In the foregoing specification I have described the auto-copy coatings consisting of either aqueous or non-aqueous suspensions as applied by either printing opera-

tions or by the conventional procedures and apparatus used in the manufacture of coated paper. The coatings, either aqueous or non-aqueous, may also be applied by casting. This method of manufacture is particularly sutiable for making the sheet of FIG. 9. In so making this sheet a transparent film-forming solution is first applied to the casting surface, which is usually a chromium plated drum, and after the film is formed but while it is still adhering to the drum a layer of coating composition is applied to the exposed surface of the film on the drum and at the same time a backing web of thin paper of contrasting color is pressed against the coating composition.

The above-described casting process is now used on a large scale in the manufacture of colored paper wherein the pigmented coating is covered with a transparent layer having a cast surface. By substituting for the conventional coating compositions now used coatings of the compositions above described, the process may be used without other change in the manufacture of auto-copy paper of the type disclosed in FIG. 9.

Instead of applying a paper backing sheet to the coating on the drum, the transparent film formed on the drum surface may be made thick enough to be self-sustaining and a backing layer of a composition such as used in the manufacture of the sheet in the manner described in column 10 may be applied to the surface of the "modified" coating while still on the casting drum.

The casting process may also be used with advantage in making the other types of auto-copy paper by substituting "modified" coatings for the conventional coatings used in the manufacture of cast-coated paper. The casting process provides a good printing surface without compacting the coating composition as is necessary when the coating is calendered.

My improved auto-copy paper may be used with advantage in the recording instruments of telautographic systems by the substitution of an electrically heated stylus for the pen or other marking instrument now used for making the record on ordinary paper. Recording instruments using ink are inherently a source of trouble, particularly where the instrument is used at irregular intervals such that the pen stands motionless for considerable periods of time. In such cases the ink tends to thicken so that although the machine operates, no record is made. With an electrically heated stylus the machine is always in working order without attention, and with my improved copy paper consisting, for example, of an underlying sheet of dark paper and an overlying layer of the formula given above as Example 1, a clear, permanent record will be made on each operation of the machine, regardless of how long the intervening idle period.

I claim:

1. An auto-copy sheet comprising a backing sheet, a continuous opaque coating of pigment particles and a binder containing a water-insoible, chemically inert, non-ionic surface active agent on one surface of said sheet, said coating being firm, dry and non-tacky and of a character such that the impact of a typewriter key under normal operation destroys the opacity of the coating in the impacted area and reveals the surface of the underlying sheet in such area.

2. The auto-copy paper of claim 1 wherein the backing sheet is paper with its surface underlying the pigment of a color different from the color of the pigment layer.

3. The backing layer of claim 1 wherein the surface-active agent is taken from the class consisting of diethylene glycol monostearate, diethylene glycol monopalmitate, pentaerythritol tetrastearate, glyceryl monomyristate, ethylene glycol monomyristate, polyethylene glycol monostearate, glyceryl monopalmitate.

4. The auto-copy paper of claim 3 wherein the surface-active agent is a monostearate.

5. The auto-copy paper of claim 3 wherein the surface-active agent is a glycol monostearate.

6. The auto-copy paper of claim 3 wherein the surface-active agent is diethylene glycol monostearate.

7. The auto-copy paper of claim 3 wherein the surface-active agent is glycol monomyristate.

8. The auto-copy paper of claim 3 wherein the surface-active agent is pentaerythritol tetrastearate.

9. An auto-copy sheet consisting of a transparent self-sustaining pliable film, an opaque coating of pigment particles and a binder containing a water-insoluble, chemically inert, non-ionic surface active agent on one side of said film, said film being of a character to be rendered transparent in limited area subjected to impact or pressure applied to the opposite side of the transparent film, and a second layer of a contrasting color overlying the first-mentioned coating and of a character to be unaffected by such impact or pressure.

10. The auto-copy sheet of claim 9 wherein the backing layer is a continuous layer of pigment particles and a bonding agent.

11. The auto-copy sheet of claim 9 wherein the second layer is a transparent film.

12. The method of making the copy sheet of claim 9 which consists in forming a transparent film on a casting drum, applying to the surface of the film while on the drum a thin layer consisting of pigment particles and an agent for rendering the layer of pigment particles resulting from the evaporation of the liquid from the carrier susceptible to impact of a typewriter key and thereafter applying to the surface of the coating while on the drum a second coating of pigment particles and a binding agent of a character to produce a layer which is not susceptible to impact of a typewriter key.

13. The method of making the auto copy sheet of claim 1 which consists in applying to the surface of a backing sheet a thin coating consisting of a liquid carrier containing a binder and pigment particles of color different from that of the underlying surface and a water insoluble, chemically inert, non-ionic surface-active agent for rendering the layer of pigment particles resulting from the evaporation of the liquid from the carrier susceptible to the impact of the typewriter key and thereafter drying said applied coating by pressing the coating layer while still plastic into adhering contact with the surface of a casting drum.

14. An auto copy sheet comprising a base sheet and a coating of contrasting color adhering to at least a portion of the surface of said sheet, said coating comprising pigment particles and a surface active agent of a character to reduce the cohesion of the pigment particles and their adhesion to the underlying sheet to an extent that the cohesion of the particles and their adhesion to the carrier are destroyed by the impact of average typewriter operation in an area co-extensive with the type, said surface active agent consisting essentially of glycol monostearate.

15. An auto copy sheet comprising a base sheet and a coating of contrasting color adhering to at least a portion of the surface of said sheet, said coating comprising pigment particles and a surface-active agent of a character to reduce the cohesion of the pigment particles and their adhesion to the underlying sheet to an extent that the cohesion of the particles and their adhesion to the carrier are destroyed by the impact of average typewriter operation in an area co-extensive with the type, said surface-active agent consisting essentially of diethylene glycol monostearate.

16. An auto copy sheet comprising a base sheet and a coating of contrasting color adhering to at least a portion of the surface of said sheet, said coating comprising pigment particles and a surface-active agent of a character to reduce the cohesion of the pigment particles and their adhesion to the underlying sheet to an extent that the cohesion of the particles and their adhesion to the carrier are destroyed by the impact of average typewriter operation in an area co-extensive with the type, said surface-

active agent consisting essentially of glycol monomyristate.

17. An auto copy sheet comprising a base sheet and a coating of contrasting color adhering to at least a portion of the surface of said sheet, said coating comprising pigment particles and a surface-active agent of a character to reduce the cohesion of the pigment particles and their adhesion to the underlying sheet to an extent that the cohesion of the particles and their adhesion to the carrier are destroyed by the impact of average typewriter operation in an area co-extensive with the type, said surface-active agent consisting essentially of pentaerythritol tetrastearate.

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