Sept. 22, 1953 J. G. ZIMMERMAN 2,653,110

MANIFOLDING TRANSFER AND METHOD OF MAKING

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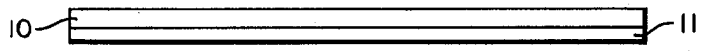


Fig. 1

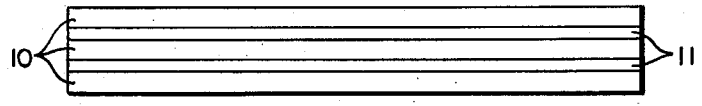


Fig. 2

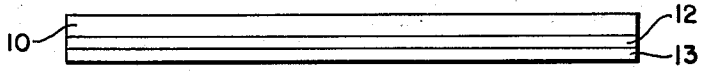


Fig. 3

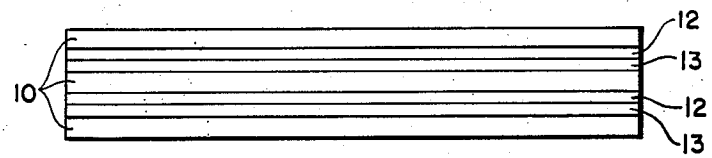


Fig. 4

INVENTOR.
JEROME G. ZIMMERMAN
BY
Tom Walker
ATTORNEY

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MANIFOLDING TRANSFER AND METHOD OF MAKING

Jerome G. Zimmerman, West Milton, Ohio, assignor to The Standard Register Company, Dayton, Ohio, a corporation of Ohio

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This invention relates to a manifolding whereby one or more copies of writing produced on an original sheet, for example by handwriting or typing, are reproduced on a copy sheet or sheets placed beneath the original sheet. Normally such copies are made by the transference of coloring matter from a transfer coating, carried either on the back of the original or duplicating sheets to an adjacent sheet or onto separate interleaved sheets.

It is an object of the present invention to provide a method of manifolding and the means whereby the use of carbon black or other dark coloring matter transfer surfaces with their attendant disadvantages is dispensed with.

It is an object of the present invention to provide a writing sheet whose transfer surface on the rear thereof has thereon two compounds capable of reacting with each other to form a dark colored sulfide under different conditions than those existing. The coating must be capable of transfer to a contiguous paper surface at the points of impression upon the reverse side of the impacted sheet.

It is more particularly an object to provide writing sheets whose transfer surfaces on the rear thereof have a colorless or light colored, substantially solid coating containing both a lead compound and a sulfide compound but which are prevented from reacting by the presence of a sufficient amount of an acidic manganese salt to maintain an acidic condition in the coating. Yet if this acidic condition were neutralized by gaseous ammonia the dark colored lead sulfide would result.

It is more specifically an object of this present invention to transfer from the transfer surface (rear surface or overlying sheet) onto the copy sheet (front surface of contiguous sheet below) colorless or light colored characters which are duplicates of those formed upon the original sheet in a typing or writing operation, and then treat the copy sheet having the imprinted colorless or substantially colorless characters containing the two aforesaid designated type chemical components with gaseous ammonia to create easily legible dark colored characters. The exposure of the colorless characters to the anhydrous ammonia (NH_3) allows the colorless lead salt present to react with the coexisting colorless, soluble sulfide because of the neutral condition.

A further object of the invention is to provide a transfer surface or coating upon a sheet of writing paper having the advantageous features and inherent meritorious characteristics as herein mentioned.

With the above primary and other incidental

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objects in view as will more fully appear in the specification, the invention intended to be protected by Letters Patent consists of the advantageous features, the components of the coating composition, and the mode of application and use as hereinafter described or illustrated in the accompanying drawing, or their equivalents.

In the accompanying drawing, which is of a diagrammatic nature,

Fig. 1 is a view of a single sheet of writing paper with the transfer surface or coating applied thereto;

Fig. 2 is a view of an assembly of superposed writing sheets forming a set of manifold record forms;

Fig. 3 is a view similar to Fig. 1, but showing a slightly modified form of the invention, and

Fig. 4 is a view of an assembly of superposed writing sheets forming a set of manifold record forms, the sheets being produced in accordance with the disclosure of Fig. 3.

Like parts are indicated by similar characters of reference throughout the several views.

According to the present invention the set of manifold material comprises a series of two or more sized sheets 10, on the rear surface of each sheet of which series (except the bottom sheet if this is undesirable) there is provided a substantially solid, uniform, colorless or very light colored coating 11 containing a metallic compound, which is capable of forming a dark colored sulfide precipitate with the co-existing water-soluble colorless sufide but for the presence of the acidic manganese salt creating an acidic condition. This coating must be transferable from the rear surface at points of impact upon the original sheet to the top surface of a contiguous paper surface in order to duplicate the imprinted characters. There is no reason actually for having the rear surface of the bottom sheet contain any coating. The transfer letters, figures, etc. are then caused to become legible by treating the copy sheets with anhydrous ammonia, i. e. NH_3 in the gaseous state.

The explanation of the formation of the dark colored, legible characters is due to the ammonia neutralizing the acidic manganese salt, such as manganous nitrate, whereby the water-soluble sulfide reacts with the lead salt present to yield black lead sulfide. Other light colored metallic compounds which may be used are those of silver, stannous tin and bismuth.

One suitable way to produce the coated transfer surface or surfaces of the sheet or sheets of this manifold system (shown in Figs. 1 and 2) is to coat the rear surface of every sized sheet of paper 10 (deducting last sheet if desired) with

an emulsion 11 containing a water-soluble sulfide and the metallic compound capable of reacting therewith to form a dark colored, insoluble sulfide but for the presence also of an acidic manganese salt which is present in an amount sufficient to create an acidic condition; this composition must be capable of drying to a fairly solid condition or state after its application. A satisfactory coating composition is an emulsion containing a volatile organic liquid, water, a water-soluble lead compound, an alkali metal sulfide, an acidic manganous salt and a polyvalent metal salt of a higher fatty acid the sulfide of the metal of which is colorless. Each of these components must be colorless or possess a light color.

It is preferred however to coat the sized sheets of paper 10 with an emulsion 12 containing the alkali metal sulfide, a volatile organic liquid and water, then after this coating has dried apply an emulsion 13 containing the water-soluble lead salt, a volatile organic liquid and water. In both emulsions a polyvalent metal salt of a higher carboxylic acid, the sulfide of the metal of which is colorless, more particularly an aluminum salt of a higher fatty acid, such as aluminum palmitate may be used. The organic liquid phase in each can be the same, but this is a matter of convenience.

The water-immiscible liquid for the emulsion or emulsions may be any suitable, volatile organic liquid such as carbon tetrachloride, benzene, toluene, etc. The polyvalent metal salt of the higher carboxylic acids may be those of aluminum, calcium or zinc. It is preferred to use aluminum stearate or the aluminum salts of other higher fatty acids; but the aforesaid metallic salts of naphthenic or the resin acids may be used. Water-soluble lead salts giving the best results are lead nitrate or the basic acetate. When the lead salts of the higher fatty acids are employed, such as lead palmitate, it is unnecessary to employ aluminum palmitate with lead nitrate or basic lead acetate. Sodium or potassium sulfides are suitable water soluble sulfides.

Bleached shellac may be added to the emulsion to alter the color and improve the texture of the coating for some varieties of paper. The more bleached shellac present the lighter the color will be. But too much will hinder the reaction. Amounts of 1–10% based on the total weight of the coating composition are usually suitable. Instead of bleached shellac other light colored natural or synthetic resins which dry to a fairly solid state can be employed.

The emulsions or dispersions herein described may be applied to various weights and qualities of sized paper having a surface which will take and hold the coatings. They may be applied in any suitable manner, such as spraying, brushing and various coating methods. The thickness will be governed partly by economic consideration but an even thin coating should be secured.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following examples which are given merely to illustrate the invention and are not to be construed in a limiting sense, all parts being given by weight:

EXAMPLE 1

Emulsion No. 1

	Parts by weight
Manganese nitrate (70% solution)	3
Potassium sulfide	2
Carbon tetrachloride	140
Aluminum palmitate	5
Water	20

These ingredients were well mixed and the resulting emulsion 12 was applied to the rear surface of the selected, sized paper. Then after drying, emulsion 13 formed from the following components was applied to the thus coated paper:

Emulsion No. 2

	Parts by weight
Lead nitrate	6
Carbon tetrachloride	150
Aluminum palmitate	6
Water	20

The treated paper was then permitted to dry.

The paper had a coating which was substantially white, solid and non-sticky or -tacky to the touch. A series of these forms was placed in a typewriter with a plain, untreated form below the last of the series. There were then typed out designated words and figures, the set of forms receiving the type blows from the typewriter, thus causing the light colored coating at the points of impact to be transferred to the underneath form. The sheets, with the exception of the top sheet which carried the original, were then exposed to dry ammonia gas (NH_3) containing a trace of hydrogen sulfide, such as 1%. The latter is not necessary but its use accelerates the reaction. As a result the previously practically invisible characters and figures became legible; they turned a semi-black color, and were clear, distinct and non-smudging. The explanation is that whereas in an acidic environment due to the presence of the acidic manganous nitrate the black lead sulfide is incapable of forming, yet in a neutralized medium it is capable.

In the above example bleached shellac can be used, being substituted up to 10% based on the total percent for the corresponding ratios of the other components.

EXAMPLE 2

An emulsion for applying as the second coating in the preferred method of securing a manifold sheet can be formed from the following composition:

	Percent
Carbon tetrachloride	74.2
Aluminum palmitate	2.45
Silver nitrate	1.65
Manganese nitrate	1.90
Shellac solution (55.6% alcohol)	3.30
Water	16.5

In other formulae, shellac was used without alcohol:

	Parts by weight
Carbon tetratchloride	3
Aluminum chloride	5
Silver nitrate	4
Manganese nitrate	4.6
Shellac (solid)	10
Water	30

Manganese sulfate may also be used instead of the nitrate. It will be understood that an emulsion containing an alkali metal sulfide (Emulsion No. 1 type in Example 1) is applied to the sized paper first and dried before the emulsion containing the silver nitrate is applied and the treated paper again permitted to dry.

It will be understood that, whereas certain specific examples have been described in the fore-

going exposition of the invention, the present invention is not limited to these but is susceptible to various modifications and adaptations, as will be apparent to those skilled in the art, without departing from the scope of the invention as stated in the appended claims. In the claims the term "colorless" is used to embrace light colored shades as well as white. In both the specification and claims the term "higher carboxylic acids" or higher carboxylate radical denotes any carboxylic acid of eight or more carbon atoms and preferably twelve or more. Where "higher fatty acids" are referred to there is meant the long chain carboxylic acids normally present as glycerides in fatty oils, and fats.

While specific materials, and proportions have been described herein, it will be understood that various changes and modifications may be made without departing from the spirit and scope of the invention. Accordingly I do not intend that my invention shall be limited to such embodiments and examples, except as hereinafter described in the appended claims.

I claim:

1. In manifolding, a sheet of sized paper on one side of which is a substantially uniform, firm, non-sticky, non-tacky, colorless coating containing a water-soluble sulfide, an acidic manganese salt in an amount sufficient to produce an acidic condition in the coating in a wet condition, said coating being characterized by the presence of a higher carboxylic acid radical in the form of a water-insoluble salt, and a metallic element of a salt, the said metallic element being capable of forming dark colored water-insoluble sulfide with the aforesaid water-soluble sulfide but for the presence of said manganese salt, and said coating being further characterized in that when said metallic element is combined as a salt which is water-soluble, the said carboxylic acid radical is combined as a salt of a polyvalent metal the sulfide of which is colorless.

2. A coated sheet of sized paper set out in claim 1 wherein the said water-soluble sulfide and the said metallic compound are present in the ratio of their chemical equivalents.

3. In manifolding, a sheet of sized paper on one side of which is a substantially uniform, firm, non-sticky, non-tacky, colorless coating containing an alkali metal sulfide, an acidic manganese salt in an amount sufficient to produce an acidic condition in the coating said coating being characterized by the presence of a higher carboxylic acid radical in the form of a water-insoluble salt, and a lead element of a salt, the said lead element being capable of forming dark colored water-insoluble sulfide with the aforesaid water-soluble sulfide but for the presence of said manganese salt, and said coating being further characterized in that when said lead element is combined as a salt which is water-soluble, the said carboxylic acid radical is combined as a salt of a polyvalent metal the sulfide of which is colorless.

4. A coated sheet of sized paper set out in claim 3 wherein the said alkali metal sulfide and the said lead compound are present in the ratio of their chemical equivalents.

5. In the process of producing a manifolding sheet the steps of coating a surface of a sized sheet of paper with a colorless emulsion of water, a water-immiscible volatile organic liquid, an alkali metal sulfide, an acidic manganese salt in an amount sufficient to produce an acidic condition, said emulsion being characterized by the presence of a higher carboxylic acid radical in the form of a water-insoluble salt, and a metallic element of a salt, the said metallic element being capable of forming dark colored water-insoluble sulfide with the aforesaid water-soluble sulfide but for the presence of said manganese salt, and said coating being further characterized in that when said metallic element is combined as a salt which is water-soluble, the said carboxylic acid radical is combined as a salt of a polyvalent metal the sulfide of which is colorless.

6. The emulsion set out in claim 5 wherein said alkali metal sulfide and the said metallic compound are present in the ratio of their chemical equivalents.

7. The emulsion set out in claim 5 wherein lead is the metallic compound capable of forming the dark colored sulfide.

8. In the process of producing manifolding sheets the steps of coating a surface of sized sheets of paper with a colorless emulsion containing water, water-immiscible volatile organic liquid, a polyvalent metal salt of a higher carboxylic acid the metallic sulfide of the metal of which is colorless, an alkali metal sulfide and an acidic manganese salt which latter salt is present in an amount sufficient to produce an acidic condition in the emulsion, permitting the emulsion coat to dry, then coating the same surface with an emulsion containing water, a water-immiscible volatile organic liquid, a polyvalent metal salt of a higher carboxylic acid, the metallic sulfide of the metal of which is colorless, and a water-soluble salt of a metal capable of forming a dark-colored sulfide with the alkali metal sulfide, when the acidic condition is neutralized, and thereafter causing the coated sheet to dry.

9. The process of making copy comprising imprinting legible characters upon the top surface of a sized paper sheet upon the rear surface of which is a substantially uniform, firm, non-sticky, non-tacky, colorless coating containing an alkali metal sulfide, an acidic manganese salt in an amount sufficient to produce an acidic condition in the coating in a moist condition said emulsion being characterized by the presence of a higher carboxylic acid radical in the form of a water-insoluble salt, and a metallic element of a salt, the said metallic element being capable of forming dark colored water-insoluble sulfide with the aforesaid water-soluble sulfide but for the presence of said manganese salt, and said coating being further characterized in that when said metallic element is combined as a salt which is water-soluble, the said carboxylic acid radical is combined as a salt of a polyvalent metal the sulfide of which is colorless, thus transferring these characters to a sheet below this coated sheet, then treating this sheet with dry ammonia gas to cause the transferred characters to become dark and legible.

10. In the process of producing manifold sheets the steps of coating a surface of sized sheets of paper with a colorless emulsion containing water, a water-immiscible, volatile organic liquid, a polyvalent metal salt of a higher carboxylic acid, the metallic sulfide of the metal of which is colorless, an alkali metal sulfide and an acidic manganese salt, which latter compound is present in an amount sufficient to produce an acidic condition in the emulsion, thereafter causing the coated sheets to dry, then coating the same sur-

face with an emulsion containing water, a water-immiscible volatile organic liquid and a salt of a higher carboxylic acid with a metal whose sulfide is dark colored, and thereafter causing the treated sheet to dry.

11. The process of making copy comprising imprinting legible characters upon the top surface of a size paper sheet upon the rear of which there are two superimposed substantially uniform and solid coatings one of which contains an alkali metal sulfide, a polyvalent metal salt of a higher carboxylic acid, the sulfide of the metal of which is colorless, and an acidic manganese salt, in an amount sufficient to produce an acidic condition in the coating the other of which coating contains a water-soluble lead salt and a polyvalent metal salt of a higher carboxylic acid, the sulfide of the metal of which salt is colorless, thus transferring these characters to a sheet below this coated sheet, then treating that sheet with dry ammonia gas to cause the transferred characters to become dark and legible.

12. The process of making copy comprising imprinting legible characters upon the top surface of a sized paper sheet upon the rear of which there are two superimposed substantially uniform and solid coatings one of which contains an alkali metal sulfide, a polyvalent metal salt of a higher carboxylic acid, the sulfide of the metal of which is colorless, and an acidic manganese salt in an amount sufficient to produce an acidic condition in the coating, the other of which coating contains a lead salt of a higher carboxylic acid, thus transferring these characters to a sheet below this coated sheet, then treating that sheet with dry ammonia gas to cause the transferred characters to become dark and legible.

13. In manifolding, a sheet of sized paper on one side of which are two superimposed substantially uniform, solid coatings one of which contains an alkali metal sulfide, a polyvalent metal salt of a higher carboxylic acid, the sulfide of the metal of which is colorless, and an acidic manganese salt in an amount sufficient to produce on acidic condition in the coating, the other of which coating contains a water-soluble lead salt and a polyvalent metal salt of a higher carboxylic acid, the sulfide of the metal of which salt is colorless.

14. In manifolding, a sheet of sized paper on one side of which are two superimposed substantially uniform, solid coatings one of which contains an alkali metal sulfide, a polyvalvent metal salt of a higher carboxylic acid, the sulfide of the metal of which is colorless, and an acidic manganese salt in an amount sufficient to produce an acidic condition in the coating, the other of which coating contains a lead salt of a higher carboxylic acid.

15. The process of producing manifold sheets set out in claim 8, wherein the last two mentioned groups of metallic compounds are present in the ratio of their chemical equivalents.

JEROME G. ZIMMERMAN.

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