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SYMPATHETIC INK

Walter S. Guthmann, Chicago, Ill.

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15 Claims. (Cl. 134—29)

My invention relates to an improved sympathetic ink and method of making and using the same.

Sympathetic inks may, for purposes of description, be considered as falling into three general groups, namely, those in which the writing is made evident by the application of heat, those in which the writing is brought out by the use of chemicals wherein a chemical reaction takes place, and, finally, sympathetic inks of a class which become visible when the paper or other medium on which they are applied is immersed in water or otherwise wetted. It is to the latter class of inks that my present invention relates.

Inks which become visible when the paper is wetted have been made heretofore. Such inks, however, have been incapable of fully successful use as printing inks, particularly for continued use on modern high speed presses. Many different types of difficulties are involved, most of which are well-known to those skilled in the art.

The principal object of my present invention is the provision of an improved sympathetic ink.

Another object is the provision of a sympathetic ink which, when applied to paper and the paper afterward wetted, will show the outline of the characters applied with the ink.

Another object is the provision of an ink of this character, wherein the characters will remain visible even though the paper may be soaked in water for a considerable period of time.

Another object is the provision of such an ink which will continue to appear and disappear even though the paper on which it is applied may be repeatedly wetted and dried.

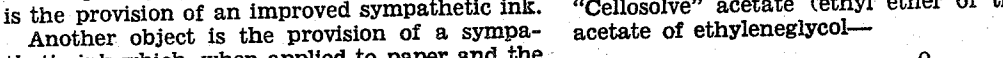
Another object is the use of a sympathetic ink of the character identified for use on either sized or unsized paper.

Other objects and features of my invention will be apparent from the following detailed description.

I shall first describe the ink of my invention as it is produced for use on unsized paper stock, such as ordinary news print, for example. For printing on this type of paper, an ink is produced which, in effect, applies a moisture resistant material having the character of a size to the portion of the paper covered by the ink, the moisture resistant material or solute material being made to penetrate the fibers of the paper and to be entirely invisible when the paper is dry. When the paper is immersed in water, however, the portion of the paper not covered with sympathetic ink is readily wetted; while the portion of the paper covered by the sympathetic ink is not readily wetted and the design of the ink is brought out plainly.

According to the preferred form of the invention, the ink consists of a material not readily wetted by water such as cellulose nitrate and a solvent having a vapor pressure range between 0.1 and 10 millimeters of mercury at 20° C. The concentration of the solute moisture resistant material in general should range from ¼% to 5%, depending upon the material and the conditions surrounding its use. The final ink is a colorless mobile liquid having the property of making the paper more resistant to wetting by water in the manner described, but being of such a nature that after it has been applied to the paper and the solvent evaporated, it leaves no mark upon the paper which can be detected by the unaided eye.

A very suitable ink made in accordance with the invention and with which I have obtained unusually good results consists of one part by weight of cellulose nitrate and ninety parts by weight of "Cellosolve" acetate (ethyl ether of the monoacetate of ethyleneglycol—



In place of the "Cellosolve" acetate, I may employ other solvents having a relatively low vapor pressure within the range indicated. Examples of such solvents are amyl alcohol, normal butyl alcohol, di-acetone alcohol, ethyl "Cellosolve" (mono-ethyl ether of ethylene glycol), ethyl "Cellosolve" acetate, methyl "Cellosolve", butyl "Cellosolve", "Carbitol" (mono ethyl ether of diethylene glycol), butyl lactate, and di-methyl phthalate. I may also use such solvents as the mixture of relatively higher boiling point solvents sold by the Du Pont Company under the trade name of H. T. P. 23, which has a vapor pressure at 20° C. of about 1.3 millimeters of mercury, and which comprises a mixture of high aliphatic alcohols and ketones from about C_4 to C_8.

Instead of cellulose nitrate, I may also employ other solute materials including other cellulose derivatives such as cellulose acetate. Certain synthetic and/or natural gums and resins can also be used such as pontianac, kauri, gum ester, ordinary rosin, etc. I may also use certain metallic soaps, such as aluminum palmitate, as well as water insoluble plasticizers, using the term plasticizer in the sense in which it is used in the varnish, lacquer, and/or paint industries. Examples are the chlorinated diphenyls, diphenyl

ethers, the condensation products of formaldehyde and thiourea, and the like.

All of the materials which I have employed successfully as solute materials are non-volatile, colorless, water insoluble, organic substances, having little or no gloss when applied in proper proportions to paper, and are capable of being deposited within the fibers of the paper in a definite, controllable outline. Some modifications in proportions of solvent may be necessary in order to insure deposition of the proper amount in the paper so that when such paper is afterwards wetted, the pattern formed by the sympathetic ink will become visible; and also so that when the paper is again thoroughly dried, the unaided eye will not be able to detect the presence of the invisible writing. In general, however, the total amount of solute sizing material in the ink should comprise at least one-quarter of one percent of the ink and should not comprise more than about five percent of the ink, the remaining portion of the ink consisting of the low vapor pressure solvent material. For general use, about one percent of solute leads to the best result.

For operating on some types of paper and under certain conditions, improved results are obtained if a mixture of more than one type of solute material is employed. For example, equal proportions of cellulose nitrate and rosin dissolved in a suitable proportion of "Cellosolve" acetate can be used with good results.

From the foregoing description, it is plain that the use of my improved ink has the effect of applying to the paper a material or substance which will affect the water permeability of the paper. When the invention is applied to paper having little or no size, my effect is obtained preferably by the use of an ink which will resist penetration of the water or, in other words, repel or resist wetting by the water while the balance of the paper is quickly permeated or saturated. Independent of the character of the solute material employed, I have found that securing of proper results, particularly when the ink is used on modern printing presses, is dependent to a great extent upon the use of a solvent having certain characteristics which I have discovered are essential.

I have found that if the solvent employed has a vapor pressure not greater than 7.5 millimeters of mercury at 20° C., the ink can be made to feed properly on ordinary high speed presses. Unless the solvent has a vapor pressure at least this low, it will evaporate on the rolls, thereby causing the ink to thicken and resulting in the deposit of too large an amount of solute on the paper. This results in the ink becoming faintly visible and therefore is objectionable for its intended purpose. With certain types of solute materials, such as cellulose nitrate or rosin, the ink also becomes sticky or tacky if the solvent has a vapor pressure in excess of 7.5 millimeters of mercury at 20° C. due to evaporation of the solvent and thickening of the ink. Under extreme conditions, this may cause a tearing of the inking rolls and also follows the type.

I have also found that suitable results are not obtained unless the solvent has a vapor pressure at least as great as 0.1 millimeter of mercury at 20° C. If the solvent has a lower vapor pressure than that given, it will have a tendency to evaporate too slowly, or even may remain in the paper almost indefinitely. It is important for proper operation that the solvent be substantially all evaporated before the paper is stacked as it is being printed. I have found that a solvent having a vapor pressure of not less than 0.1 millimeter of mercury, when used in the amounts required, will evaporate with sufficient rapidity. A solvent material like glycerine, for example, is not entirely satisfactory because of its extremely low vapor pressure and also because of its hydroscopicity.

The solvent employed must also have a surface tension sufficiently low to permit its penetrating the fibers of the paper. In general, I have found that the surface tension should be at least as low as water under comparable conditions in order for the relatively small amount of solvent applied to the paper to penetrate the fibers thereof and carry the solute material with it before it evaporates. The solvent employed must also be compatible with water to such an extent that a relatively slight amount of moisture on the paper will not repel its penetrating action. If the ink is not compatible with moisture in relatively small amounts, different results will be obtained during different weather conditions. As an example, commercial naphthas may be obtained having a vapor pressure of about four millimeters of mercury at 20° C., which in many respects will be expected to be suitable solvents for use in the ink of my invention. I have found, however, that these naphthas seem to be repelled by only very slight amounts of moisture which are found on the surface of the paper on a damp day. I have found also that the surface tension of these naphthas is not sufficiently low to cause a penetration of the fibers of the paper. Other examples of solvents unsuited for use in my invention could be given, but it is not believed that further examples will add to the disclosure.

The use of a solvent having the characteristics of relatively very low vapor pressure, relatively low surface tension, and compatibility with slight traces of moisture, all co-operate to cause a quick penetration of the fibers of the paper, thus avoiding the deposit of the solute material on the very outside surface of the paper and at the same time reducing the tendency to form a gloss which could be detected by the unaided eye when the paper was in a dry state. By establishing a lower limit of vapor pressure, sufficiently rapid evaporation is obtained. The result is that during the relatively short space of time between printing and stacking, the ink is caused to penetrate the paper and the solvent at the same time is given an opportunity to evaporate.

While I have given a vapor pressure range between 0.1 millimeter of mercury at 20° C. and 7.5 millimeters of mercury at 20° C., it is to be understood that this represents a workable range which I have determined by numerous experiments. I prefer, however, to employ a solvent having a vapor pressure of approximately one millimeter of mercury or to establish a closer range, between .5 and 1.5 millimeters. I have found that a sympathetic ink employing a solvent within this range is capable of general use on substantially all types of press equipment. An ink employing a solvent having a higher or lower vapor pressure than about one millimeter of mercury may be limited in its application. For example, I have produced an ink employing a solvent having a vapor pressure of four millimeters of mercury at 20° C. which is satisfactory for presses such as a Gordon press. The same ink cannot be used with full satisfaction, however, on a Miehle type of press. An ink employing "Cellosolve" acetate (vapor pressure 1.26 millimeters of mercury at

20° C.) is very satisfactory on a Miehle type of press, but can also be used on a Gordon press. Indeed, I have found that this particular solvent can be used successfully in an ink intended for use on any type of press with which I am familiar.

The inks described above are liquid and are best employed by the use of a fountain arrangement such as that described in my co-pending application Serial No. 741,929, filed August 29, 1934. I may, however, compound such inks so that they will have approximately the same consistency as standard printing inks. By the use of a relatively small amount of a water insoluble soap, the ink can be produced in the form of a gel having the consistency desired. The proportion of soap used varies with the amount and character of both the solute material and solvent, and also depends upon the consistency of the gel desired. In general, I do not prefer the use of this character of ink, however, on unsized paper, because of the difficulty of securing adequate penetration into the fibers of the paper. An ink of this kind may be readily made which may be thoroughly satisfactory on one type of paper but as soon as the paper is changed, a trace of the ink markings may be visible when the paper is dry. It should be noted that I may employ certain metallic soaps alone as the solute material, in which case a liquid ink may be produced.

When printing on bond paper or similar sized paper, the ink may be modified, if desired, by causing the portion of the paper covered with the ink to become more permeable to moisture instead of rendering it less permeable. When using bond paper, it is not so necessary to cause a deep penetration of the fibers as is the case when an unsized paper is used. I find that suitable results may be obtained on bond paper if the ink is produced in the form of a gel having substantially the same consistency as ordinary printing inks. In its preferred form, the modified ink comprises a solid material acting as a penetrating agent to facilitate penetration of the paper by water, and a solvent material having a vapor pressure range of between 0.1 and 7.5 millimeters of mercury at 20° C. I have found, however, that the vapor pressure is not as critical as in the first modifications of the invention and, even though the vapor pressure of the solvent is not within the extremely narrow range preferred in the first example, the ink may still be used with considerable latitude as to type of presses and character of paper.

As penetrating agents, I may employ ordinary soap such as white castile soap and/or substantially non-oleaginous wetting agents such as the "Gardinols" and "Avirols" which are the sulphuric acid esters of the higher fatty alcohols and their salts such as lauryl sodium sulphate and cetyl sodium sulphate; and "Igepons" which are compounds of the following structural formulae:

$$R—CO—O—C_2H_4—SO_3X$$

$$R—CO—NH—C_2H_4—SO_3X$$

wherein R is an alkyl radical having from twelve to eighteen carbons, and X is hydrogen or a cation such as sodium, and similar wetting and penetrating agents of commerce. It will be noted that the "Igepons" are higher fatty acids or higher fatty acid amides wherein the hydrogen of a carboxyl or amino group is substituted by an ethionic acid radical. When employing the soap with another penetrating agent, the function of the soap is principally to produce the gelatinizing action. Some of the penetrating agents with certain solvents may also have the same effect. My preferred solvent for this character of ink is cyclohexanol, although other solvents may also be used. This ink may have such a consistency that it may be used according to the process and employing the apparatus described in my co-pending application, in which case the soap is not used in the formula. It may also be used in the same way that ordinary printing inks are used without producing a visible mark when the paper is dry.

It is not to be understood that the ink produced in accordance with the first modification of the invention is limited only to unsized paper and that the ink made in accordance with the latter modification can be used only with fully sized paper. There is a very large amount of paper used in the printing industry which is only partially sized. An example is the so-called English finish, well-known in the printing trade. On paper of this character, either type of ink may be used. On paper of this kind, I may use both inks together by making separate impressions, one with each ink, and so secure very novel effects which could not be obtained by the use of either ink alone. Pictures such as likenesses of persons requiring modifications in shade can be produced with very artistic effects.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A sympathetic ink, normally invisible when applied to dry paper of sized or unsized type but adapted to be made visible when the paper is wetted, said ink comprising a material affecting the water permeability of the paper, and a solvent therefor having a vapor pressure between approximately 0.1 and 7.5 millimeters of mercury at 20° C., said material constituting on the order of 0.25% to 5% of the composition.

2. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising a moisture resisting substance, and a solvent therefor having a vapor pressure of not less than 0.1 millimeter and not more than 10 millimeters of mercury at 20° C., said substance constituting on the order of 0.25% to 5% of the composition.

3. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising a moisture resisting substance, and the ethyl ether of ethylene glycol mono-acetate, said moisture resisting substance constituting on the order of 0.25% to 5% of the composition.

4. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising about one percent of a substantially colorless moisture resisting material and a solvent therefor having a vapor pressure between approximately 0.1 millimeter and 7.5 millimeters of mercury at 20° C.

5. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising a relatively small amount of cellulose nitrate and a solvent having a vapor pressure between approximately 0.1 millimeter and 7.5 millimeters of mercury at 20° C., the cellulose nitrate constituting on the order of 0.25% to 5% of the composition.

6. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising a material for modifying the water permeability of paper, and a solvent having a vapor pressure

not greater than 7.5 millimeters of mercury at 20° C., a surface tension not greater than that of water under identical conditions, and compatible with relatively small amounts of moisture whereby the solvent is adapted to carry the material for modifying the permeability of the paper into the fibers thereof, said solvent having a vapor pressure of not less than 0.1 millimeter of mercury at 20° C. whereby during a printing operation said ink may be permitted to dry before the paper is stacked, said material constituting on the order of 0.25% to 5% of the composition.

7. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising a non-volatile, colorless, water insoluble organic substance of a film-forming class of substances consisting of cellulose esters, gums, and resins, and a solvent having a vapor pressure of between 0.1 and 7.5 millimeters of mercury at 20° C., with a surface tension not substantially greater than that of water and having compatibility with water in relatively slight amounts whereby the solvent may carry the solute material into the fibers of the paper, said substance constituting on the order of 0.25% to 5% of the composition.

8. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink consisting substantially of a colorless, water resisting material, a solvent therefor having a vapor pressure between approximately 0.1 millimeter and 7.5 millimeters of mercury at 20° C., and a metallic soap in sufficient amount to cause the ink to take a plastic form due to the gelatinizing action of the soap, said water resisting material constituting on the order of 0.25% to 5% of the composition.

9. A sympathetic ink for application to bond or sized paper, said ink being normally invisible when applied to the paper but adapted to be made visible when the paper is wetted, said ink comprising a penetrating agent and a solvent therefor having a vapor pressure between approximately 0.1 millimeter and 7.5 millimeters of mercury at 20° C., said penetrating agent constituting on the order of 0.25% to 5% of the composition.

10. A sympathetic ink for application to bond or sized paper, said ink being normally invisible when applied to the paper but adapted to be made visible when the paper is wetted, said ink consisting substantially of soap, a penetrating agent, and a solvent therefor, said ink being in plastic form, the penetrating agent constituting on the order of 0.25% to 5% of the composition and the soap being present in sufficient proportions to impart a plastic form to said ink.

11. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink consisting substantially of a moisture resisting substance and a solvent therefor of a class consisting of alcohols and ethers, said solvent having a vapor pressure between approximately 0.1 and 10 millimeters of mercury at 20° C., said moisture resisting substance constituting on the order of 0.25% to 5% of the composition.

12. A sympathetic ink, normally invisible when applied to paper but adapted to be made visible when the paper is wetted, said ink comprising cellulose acetate and a solvent therefor having a vapor pressure between approximately 0.1 and 7.5 millimeters of mercury at 20° C., the cellulose acetate constituting on the order of 0.25% and 5% of the composition.

13. A sympathetic ink for application to bond or sized paper, said ink being normally invisible when applied to the paper but adapted to be made visible when the paper is wetted, said ink comprising a solution of lauryl sodium sulphate in di-acetone, alcohol, the lauryl sodium sulphate constituting approximately 5% of the composition.

14. A sympathetic ink for application to unsized paper, said ink being normally invisible when applied to the paper but adapted to be made visible when the paper is wetted, said ink comprising a solution of nitrocellulose in ethyl ether of ethylene glycol mono-acetate, the nitrocellulose constituting approximately between 1% and 2% of the composition.

15. A sympathetic ink for application to bond or sized paper, said ink being normally invisible when applied to the paper but adapted to be made visible when the paper is wetted, said ink comprising a penetrating agent of a class consisting of sulphuric acid esters of higher fatty alcohols and ethionic acid derivatives of higher fatty acids and higher fatty acid amides, and a solvent having a vapor pressure of between approximately 0.1 millimeter and 7.5 millimeters of mercury at 20° C., said penetrating agent constituting on the order of 0.25% to 5% of the composition.

WALTER S. GUTHMANN.