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INK ADJUVANTS

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This invention relates to adjuvants for printing inks, particularly overcoming smearing of freshly-printed sheets. This composition is intended for printers, as contrasted with manufacturers, to add to inks; though manufacturers may do so. Hence the mode of application must be both simple and effective even with inks of various sorts and sources.

The invention is illustrated by reference to planographic printing inks. These print separate sheets of paper fed through a printing machine. Advantages appear also with other types of ink. The art will recognize that in lithography, for example, separate sheets are printed and then stacked in rapid succession before the ink is really dry. Frequently ink from a freshly-printed sheet blurs the characters or smudges an adjacent sheet. This is termed offsetting.

Various attempts in the past to combat offsetting have been unsatisfactory, for one reason because of the time element. The remedy should act almost instantaneously, as the printed sheets pile up at high speed. Thus, to blow powder upon each fresh sheet or to blow hot air across the sheet are too slow and inherently too late. The same is true of trying to evaporate a component by heat before the paper smudges. The ink, when printed on the paper sheet, should change at once to a smudge-resisting film.

The present invention provides an anti-offset agent with inks based on drying oil. Such well-known oils are various vegetable oils, notably linseed oil. One authority (Mattiello, Protective and Decorative Coatings, vol. III (1943), page 620) states, "Lithographic varnishes are heat-bodied linseed oils whose viscosity has been increased by heat-processing the raw oil." Also, page 636, "Although linseed oil, as lithographic varnish, is chiefly used, perilla and tung oils are also employed."

In part this invention is to provide an anti-offset agent that mixes easily into such ink, as for example into lithographic ink paste. A special purpose is to provide an additive that is free from dangerous or combustion-promoting components. Another object is to provide an additive that leaves the ink free from stringiness or such tackiness as would form fine smudge lines on the sheets. Specific illustration will make these and other objects clear to those skilled in the art.

An over-riding purpose in general is that the additive and ink composition shall set instantly on printing, yet be of a character to avoid gumming in the machine before printing. A further purpose is that this quick-setting composition shall require no evaporation nor addition on printing.

In the following description and claims the percentages expressed are by weight.

Many advantages of this invention result from a composition of starch and water combined with partly oxidized (that is, heat-bodied) drying oil as a composi-

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tion to be added to ink. Various proportions may be used, but particularly desirable results follow with water in proportion to starch in a range of about 85% to 150%, with the oxidized oil about 10% to 30% of the starch, or about 5% to 15% of the additive. A preferred composition of about equal parts water to starch within these ranges is 15 ounces of water, 16 ounces of starch. In this are 3 ounces of lithovarnish No. 1 or lithovarnish No. 2, which are medium lithovarnishes. In this preferred example the water is about 95% relative to the starch and the oxidized linseed oil about 20% relative to starch. In this specific example, then, relative to the additive itself, the starch is 46.5% of the additive, the water 44.2% and the lithovarnish 9.3%. No. 1 varnish is preferred. Lithovarnish is partly oxidized drying oil, usually linseed oil. There are several such grades or numbers of lithovarnish, as the art knows, characterized by differing degrees of oxidation or corresponding polymerization, viscosity, acidity, specific gravity and other qualities. In one system of nomenclature, these are numbered from 0 to 9. The No. 1 lithovarnish, regular, has a specific gravity of 0.96 and viscosity of 26.0 poises (as compared to raw linseed oil of 0.5 poise); while No. 2 lithovarnish has a specific gravity of 0.97 and viscosity of 32.8 poises. The starch in the additive may be various sorts, such as corn starch, potato starch or even starches modified by heat, hydrolysis or halogenation for example. However, unmodified starch, being of non-ionic or slightly anionic character, is preferred because of its electrostatic qualities in the ink in which it is to function.

The additive composition in simplest form is prepared by vigorously agitating the starch, water and lithovarnish together. Evidently this yields an emulsion of oil-in-water type, appearing like water but with droplets of the lithovarnish suspended in water. Also the starch particles are distributed throughout the water. More detailed description of this preparation is not necessary, as those skilled in the art will be able to follow this description.

For use, the printer simply places a small amount of this additive composition in contact with the ink to be printed and mixes it in directly, for example with a spatula or with any casual mixing machine. This is to say that elaborate or vigorous mixing means are not needed. As a matter of fact use of commercial ink-manufacturing processes or machinery such as rolls or grinders tends to destroy the additive of this invention, whether by heat, pressure, incorporation of pigments, or the like. This additive blends easily with the ink. As an example of quantities, 2 to 5 ounces of the additive blend suitably with 5 pounds of ink; that is the order of 2% to 6% of additive relative to the ink. This averages about 3.5% of the ink being an emulsion of starch and water in about equal proportions. In broad limits the ink receives about 0.1% to 1% of lithovarnish from the additive. It is evident that this blending is facilitated, in the nature of the compositions, by a phase reversal of the additive. The ink comprises a base or general medium of oil which in lithographic ink usually is vegetable oil. The additive, containing oil droplets as internal phase in water, reverses so that the oil droplets readily disperse in the ink oil medium and bring the water and

starch into the ink. Thus water and starch particles or droplets readily distribute throughout the ink. Of course the ink contains various other components usual to the particular ink; namely, pigments, resins and others, as in known to those skilled in the art. That is, this additive is applicable generally to various inks, particularly lithographic inks. Applicant is not limited to any particular theory of action, but regards the foregoing explanation as accounting for the ready assimilation of this additive in the ink and for its subsequent efficacy against offsetting.

Finally the lithographic ink containing additive is applied and printed as usual in this art. Fluidity of the ink awaiting printing is not altered materially nor is stringiness developed. No particular solvents are needed, yet the printed character takes sufficient body immediately on printing that smudging is avoided.

Applicant views this improvement as the result of technical actions within the ink. These become effective on printing. Probably they are complex actions, despite apparent simplicity of the additive and its combination with the ink. Before outline of these views, it is preferable to describe an improved form of this additive. The additive however is an emulsion or suspension in water; that is, a water base in which are suspended starch and lithovarnish.

In this second form, applicant combines with the described emulsion of lithovarnish and starch in water a small amount of polymerized cellulose ether. This is sometimes popularly denoted as gum but more exactly is a polymer of cellulose ether. Such are known of themselves as being cellulose in which hydrogen of an OH group is replaced to give an alkoxyl compound. Replacement may be by an alcohol residue, yielding for example ethyl or methyl cellulose ether, or by an acidic residue to give a carboxy ethyl or methyl cellulose ether, for example. An example of the carboxy ethyl compound is known commercially as 4400 gum; an example of the methyl compound is known as CMC or (sodium) carboxymethyl cellulose, from a methylacetic residue.

As an example of this modification of the invention, an amount of 2.5% of 4400 cellulosic ether gum in water is prepared (or more broadly 0.5 to 3% gum). Then 32 ounces of this are mixed with from 0.5 to 3 ounces of lithovarnish No. 1. This lithovarnish may range in the order of 0.5% to 5% of the adjuvant, preferably about 3%; or about 2% to 15% or preferably about 10% to 15%, or more specifically the order of 10% relatively to added starch. Mixing is accomplished preferably in a high speed mixer or such as to obtain a milky or emulsion preparation. Twenty-four ounces of powdered starch are mixed in until a smooth and apparently uniform fluid is obtained. Thus in this example of the adjuvant composition water is substantially 133% relatively to the starch. Otherwise stated, in this example of water containing 2½% ether gum and 0.5 to 3 ounces of heat-bodied lithovarnish oil, this adjuvant composition is about 55.2% to 53% water, 42.5% to 40.6% starch, 0.9% to 5% lithovarnish oil, and about 1.4% cellulose ether gum. The cellulose ether gum may range about 0.5% to 3% of this adjuvant, preferably about 1.5%. Temperature of the liquid to facilitate starch dispersal should be warm, say above 50° F. but not exceed about 100° F. during the preparation. If desired 0.5% of a fungicide may be added at any time for future preservation of the starch combination. Choice of fungicide may rest with the producer of this ink additive; suitable examples are Antara Preventol or Dowcide A, or PMA 30 (phenylmercuric acetate). The additive is now ready for use and will not require stirring anew.

As a further example, either preparation described may contain some drier. About 3% of cobalt drier is satisfactory. This would have been added during the mixing already described. However, drier is not necessary.

As alternative in either broad example given, all the

components may be added together and distributed by vigorous agitation. This is facilitated by a small amount of wetting agent. Such agent serves also later to keep ink from piling up on the distributing rollers. One suitable example is known as NPX, which is a tergitol wetting agent. An illustrative portion is about 45 grams to 15 gallons of ink.

The balances of the adjuvant under this invention are sensitive even to differences in dryness of paper between summer and winter. In winter when paper is drier, the adjuvant desirably should contain about two to four percent more water than in summer.

In use, the lithograph operator simply adds from one to three ounces of the aqueous emulsion adjuvant containing starch, cellulose ether and lithovarnish to about four (thus being about 1.6% to 4.7%) or five (thus being 1.2 to 3.7%) pounds of ink, and knifes them together on the usual ink slab. For coated offset paper stocks, about 1 to 3 ounces of this adjuvant are used with 5 pounds (thus being about 1.2% to 3.7%) of ink; for plain offset stocks, about 3 to 4 ounces are preferred with 5 pounds (thus being about 3.7% to 5%) of the ink. In this range of examples the additive is of the order of about 1% to 5% of the ink. Relative proportions of the additive components within the ink are substantially the same numerically as in the previous example. In these examples, in the additive the starch is about 39 to 46%, water 44 to 52%, lithovarnish 5 to 9%, and cellulosic ether gum 0 to 4%. Hence, relatively to the ink containing about 1% of additive, these components are about: starch 0.4 to 0.5%; water 0.4 to 0.5%; lithovarnish 0.05 to 0.10%; cellulosic ether gum 0 to 0.04%. Where the additive is 6% of the ink, these components, then, are of the order of: starch 2 to 3%; water 2 to 3%; lithovarnish 0.3 to 0.6%; cellulosic ether gum 0 to 0.25%. Thus substantially the lithovarnish will be of the order of 0.05% to 0.6% or even 1% of the ink, the cellulosic ether gum about 0 to 0.25% of the ink, the starch and water in about equal quantities together being about 0.8% to 6% of the ink.

The water is extended by the starch. The starch, or the starch and gum together, as the case may be, within the water now emulsified within the ink are in excellent position to respond to even slight withdrawal of water. This condition obtains throughout the ink, though the individual aqueous particles, being in emulsified condition, are themselves exceedingly tiny. This is a metastable condition. The cellulose ether is relatively slight, of the order of 0.05% of the ink where 3 ounces of adjuvant were added to five pounds of ink. The additive is of a pasty consistency but on mixing thins readily into the ink. The lithovarnish in the additive facilitates this mixing of the aqueous starch paste or the starch and gum paste into the ink, despite the predominance of water in the additive and predominance of oil in the ink. As indicated earlier, this varnish appears to facilitate a reversal of phase during the mixing of additive with ink. As a result, the ink at the time of printing contains aqueous starch particles distributed throughout the ink matrix of oil. The cellulosic gum when present is slightly soluble in water and of such character as to aid colloidal distribution or peptization of the starch in water and thus maintain fluidity.

With respect to the actual mechanism making this additive effective, applicant desires not to be bound by theory. Nevertheless, certain aspects of operation do appear to be consistent with the following views. First, it is clear that desirable properties of the additive comprise its adaptability to two distinct spheres of operation. One is its long shelf life, maintaining a distinctly aqueous character even though containing oil (lithovarnish) and maintaining ability to be knifed easily into lithographic ink. The other sphere of operation is after distribution into the ink; on printing the combined ink instantly functions to re-

press offsetting or smudging. The actions involved undoubtedly are complex.

Ultimate setting of the ink after printing is of less immediate interest than the instant toughening or setting of the outer surface of the printed character.

Ink containing this adjuvant is an oil vehicle, particularly a drying oil vehicle holding suspended starch and water particles more or less bound together. In the form containing the cellulosic gum, this gum in water is distributed throughout the oil and apparently distributed throughout the starch-water particles themselves. This cellulose ether undoubtedly is adsorbed on the starch, tending to trigger the entire complex to gel when its water balance is destroyed.

In printing, by one method or another, pressure converts a small mass of ink into a film pressed upon a surface. This surface usually is fibrous, and usually of carbohydrate fibres such as wood pulp or cotton. It may be more or less coated, but is hydrophilic. Paper of this sort will be taken here as illustrative, though advantages of the invention are found with other hydrophilic bases as well.

The pressure of printing, whether assumed to be slight or great, is considerable as bearing upon the internal flow of an ink droplet during printing. The droplet is suddenly sheared and left as a relatively flat film upon the paper. At the instant it is wet. It changes quickly, under this invention, to a tough surface, without added heat and without extraneous material added. At the moment of printing, distribution of aqueous phase throughout the oleous base is extensive. Then two forces are brought into play; the attracting or imbibing effect of the paper fibre for water and the colloidizing effect of the de-watered starch. This becomes a matter of water distribution. There is also a tendency for the starch particles to move away from some papers to the exposed surface of ink. As a result there is an instantaneous withdrawal of water from the ink, an increasing concentration of starch at least relative to water, and immediate gelation in the outer surface of the printed film. This gelation becomes apparent as increased tenacity or firmness of the ink surface which may or may not extend to its own interior mass. This is sufficient to accomplish the purpose of this invention in overcoming offsetting.

In cases where cellulose ether gum is present, this ether is sufficiently soluble in water and sufficiently adsorptive to the starch to emulsify, or suspend, the starch in water within the general environment of the oily vehicle of ink. This improves both fluidity and stability of the ink until printed. But on contact with paper, instantaneous removal of water into the paper sufficiently decreases the solution of cellulose ether to release its suspending action on the starch. In consequence the starch gels at once in the ink. This is similar to action of the starch in the first example but aided by the triggering action of the cellulose ether.

Viewed as electrostatic or polar action and redistribution between the surfaces present when the ink is printed, the antioffset nature of the ink with adjuvant is consistent and clear. The paper being printed is frequently anionic. Also it is of a character to attract water and water containing cellulose ether. Starch also is anionic and tends to move away from anionic paper to the outer surface of the printed ink film. This is a concentrating tendency. Because of it the starch, or starch and cellulose ether, agglomerate or gel. A small proportion of the ether of the order of one-tenth of one percent or even less, is sufficient. Withdrawal of a minute amount of water exerts multiplied effects that result in this gelation. This is sufficient for the purposes of this invention.

It will be apparent to those skilled in the art that the fibres on which the printing is done may be coated fibres so long as the fibres absorb water. In general the printed surface need be only one that imbibes or attracts water. Thus synthetic fibres, silicone fibres and ceramic fibres,

when made into a hydrophilic printing surface may be lithographed to advantage under this invention. Letter press printing is improved under these principles. Other departures from the strict letter of the examples given will also be apparent. Thus water may be replaced to greater or less degree by liquids that are attracted by the printed surface and imbibed thereby. This is something other than mere percolation into the interstices of the fibrous surface. The action desired is to withdraw the liquid that wets or dissolves starch or starch and cellulose ether, so that gelation results when the ink is printed.

In compliance with the patent statutes, this invention has been set forth in terms of the best mode of operation now known. Its principles of practice have been illustrated so that those skilled in the art will perceive various advantages of this invention and extensions thereof beyond the illustrations and specific materials of this description within the limits of the appended claims.

What is claimed is:

1. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of a water base in which are suspended starch and heat-bodied lithovarnish drying oil, the water being substantially 85% to 150% relative to the starch, the composition having the property of being miscible directly with oil-base printing ink.

2. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of an aqueous suspension of starch and heat-bodied lithovarnish drying oil, the proportion of water being about 85 to 150% relative to starch and the lithovarnish oil being about 10 to 30% relative to starch.

3. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of an aqueous suspension of starch and heat-bodied lithovarnish drying oil, the proportion of water being about 95% relative to starch and the lithovarnish oil being about 20% relative to starch.

4. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of starch and water in about equal quantities, and suspended therein heat-bodied lithovarnish oil of viscosity about 25 to 33 poises.

5. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of a water base containing starch, the proportion of water being about 85% to 150% relative to the starch, and heat-bodied lithovarnish oil suspended in the water base, the base also containing about 0.5% to 3% of cellulose ether relative to the water.

6. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of a water base containing starch and cellulose ether and heat-bodied lithovarnish oil suspended in the water, in proportion to starch the water being about 85 to 150% and the lithovarnish oil being about 2% to 15%, the said oil being about 0.5% to 5% of the adjuvant, the cellulose ether being about 0.5% to 3% of the adjuvant.

7. An improved composition of matter, useful as an adjuvant for imparting anti-offset properties to oil-base printing ink, substantially the entire composition consisting essentially of about 1.5% cellulose ether and a water base with starch and with heat-bodied lithovarnish oil of viscosity about 25 to 33 poises suspended in the water, the water being about 95% and the lithovarnish being about 10% to 15% relative to the starch.

8. Printing ink of drying oil base having suspended

therein water particles containing starch, the water being about 85% to 150% relative to the starch, the starch and the water together being about 1% to 5% of the ink.

9. Printing ink of drying oil base having suspended therein water particles containing starch, the water and starch being in about equal quantities to each other and being together about 3.5% of the ink.

10. Printing ink of drying oil base having suspended therein water particles containing starch, the water being about 85% to 150% relative to the starch, water and starch being together about 1% to 5% of the ink, the ink containing also cellulose ether about 0.5% to 3% relative to the water.

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