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PLANOGRAPHIC PROCESS AND INKS

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This invention relates to improved planographic inks and method of employing same. More specifically, this invention is concerned with incorporation of certain silica additives into planographic inks whereby their use in a planographic printing process is improved to a considerable degree.

The planographic process, considered one of the major divisions of printing, includes such processes of printing as stone lithography, offset lithography, offset tin printing, heat-set web offset printing, etc. In each of these processes, the operation is generally accomplished by having ink-receptive and ink-repellent areas on the printing surface or plate. In their broadest aspect, these processes generally consist of preparing a slightly etched plane surface having both ink receptive and ink repellent areas and then treating this surface with both an aqueous liquid and a planographic ink. The planographic ink then is selectively received by the ink receptive area, or hydrophobic area, while repelled by the hydrophilic area which attracts the aqueous liquid. The treated plate then is contacted with a paper sheet whereby an inked impression is produced. The plane surface of the metal plate used to transfer the image to the paper may include both flat and curved metal plates.

For example, in the ordinary stone lithographic process a design is placed upon the smooth surface of the stone either by means of a pen or brush or greasy crayon, known as lithographic chalk, or from a previously prepared design through use of suitable transfer paper. The stone is then treated with a gum solution which is later washed off the design but left on those portions which are not to print. Heavy ink is then applied which adheres only to the design. This is followed by an etching operation which acts only on those portions of the stone which have not been previously protected by the heavy ink. The etching is carried out in order to make the inked portions stand out sharply and in slight relief. When the stone is ready for use, fountains are filled with ink and water and paper sheets are fed to contact the stone much the same as in a cylinder press. Generally the stone itself is kept damp by means of rollers wetted by the fountain solution.

Offset printing is essentially the same type of process as stone or other types of lithography with the exception that the printing is effected from curved metal plates. In this process the ink is transferred from an etched metal plate to a rubber blanket and then "offset" to the sheet to be printed. Here a sheet of either aluminum or zinc is properly grained, the design to be printed transferred to the grained metal by several methods such as by means of transfer paper. In another method, the grained plate or sheet is phototreated by contact with a solution of albumin and glue or gum Arabic sensitized with ammonium bichromate whereby a coating is produced, which coated plate is then exposed to arc lamps. After treatment with a developing ink and subsequent counter etching, the plate is then available for mounting on the printing press. Other well-known processes of preparing plates are by preparation of deep-etched plates and multi-metal plates which all depend upon photographic means for forming images upon the plates.

One of the newest planographic printing processes

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which is finding increased use particularly during the last decade is a method known as heat-set web offset printing. This has an advantage in that the paper may be fed in a continuous roll and both sides of the web or sheet may be printed simultaneously. In this method generally durable printing plates such as bi- and tri-metallic plates are used. Also, deep-etched plates, particularly copperized aluminum plates may also be used. Here for example, an aluminum plate is electroplated with copper, sensitized and exposed behind a photographic negative. After exposure and development the copper is etched away from non-image areas, exposing the aluminum in those areas. In the printing process the copper is ink-receptive and the aluminum water-receptive.

During the printing process itself the plate is kept dampened with water from a water fountain which selectively wets the aluminum area of the plate. The ink is transferred from a roll to the plate and deposits only where the copper is located. The impression from the curved plate is then transferred to a rubber transfer roll which in turn transfers the impression upon the paper which is subsequently heated to quickly dry the ink. A series of these contacts may be made in succession whereby various colors are imparted to the paper. Thus, such a process is particularly desirable where colored picture or other color reproductions are desired. In all of these processes, it is essential to keep a tightly controlled hydrophobic-hydrophilic balance. That is, since the ink and water come into intimate contact with each other, it is necessary that they be in the exact proper condition of hydrophobicity or hydrophilicity. For example, if the ink is not sufficiently hydrophobic, many undesirable situations may take place. For example, emulsification of the water by the ink might occur thereby causing diluted light colors, poor drying, undesirable viscosity changes, etc. Likewise, if the ink is overly hydrophobic it tends to repel the water at the plate and causes poor resolution of the printing. Thus, in the above situations, the images tend to wander and cause frequent shutdowns with costly production and labor losses.

In many instances without benefit of adequate additive treatment, planographic inks are frequently susceptible to the above deleterious circumstances occurring during the planographic process. In many cases, use of some planographing inks must be rejected due to the fact that they are susceptible to harmful physical and chemical changes when coming in contact with water, and particularly when they are emulsified in presence of water either fed through fountains or by means of dampened rollers. This emulsification frequently causes bleeding into the un-inked portions of the form or plate and tints the printed sheets.

It would therefore be an advantage to the art if an additive could be found which helps maintain the hydrophobic-hydrophilic balance of a planographic ink, substantially inhibits emulsification tendencies, and yet does not change to any substantial degree the rheological properties of the ink. It would be a further advantage if such an additive could be used in a variety of planographic inks and in any of the various planographic processes.

It therefore becomes an object of the invention to provide planographic ink compositions containing an additive whereby improved properties are achieved.

Another object of the invention is to provide a variety of planographic inks which may vary widely as to their particular constituents, which additionally contain a specifically modified silica additive which is of such physical and chemical character that it can be uniformly dispersed

throughout the ink and remains stably dispersed for long periods of time.

Yet another object of the invention is to provide a method of improving the overall planographic process by use of planographic inks containing specific silica additives.

In accordance with the invention I have discovered that planographic inks may be considerably improved by incorporation therein of organo dispersible silica particles having an average diameter of from about 5 to about 150 millimicrons and having a chemically bound organic hydrophobic surface coating. Incorporation of the silica additive helps to maintain the desired hydrophobic-hydrophilic balance in the ink, thereby causing sharply defined areas of ink concentration and aqueous liquid concentration on the printing plate. Such effect likewise causes the impression as reproduced upon the paper to have sharp limits of definition without any tendency of "wander."

In particular, a planographic ink having the organic coated silica incorporated therein has no tendency to cause emulsification of water into the ink with the result that there is no bleeding of the water into the hydrophobic ink substance, producing blurred images on the paper or tinting of colors.

I have also discovered that the planographic process itself may be measurably improved by such above-stated incorporation of additive into the planographic ink. In particular, since untreated planographic inks often emulsify and thereby become excessively viscous, the speed of the planographic process must necessarily be diminished to compensate for such increase in viscosity. Therefore, incorporation of the additive which tends to limit emulsification problems to a bare minimum, likewise does away with problems of viscosity increase and allows the proper optimum operational speed. This is particularly critical in such areas as heat-set web offset printing where a continuous paper roll is fed at rates much higher than was heretofore possible in previous decades.

SILICA ADDITIVES

As broadly described above the silica additives of the invention have a coating of organic material around a core of dense silica particle making them extremely hydrophobic in nature. Also, this surface coating is connected through chemical means, that is, is chemically bound to the silica rather than existing as a mere physical coating of the core which may be more easily removed. The organic coating is bound to the silica particles by means of siloxane bonds which are formed by reaction of an organic substance such as an alcohol with the silanol groups of the silica particles. The organo-coated silica substances are of colloidal dimensions and have ultimate particle diameters no larger than 150 millimicrons. The lower range of diameter on the average is about 5 millimicrons. This property of being colloidal in nature is necessary so that the coated silica particles may be uniformly dispersed in the hydrophobic planographic ink and also stably remain in such condition during such time as the ink may be kept in storage prior to actual use or in a suitable container or fountain during the actual time of the process itself. Particularly, when the planographic ink is transferred as a thin film upon the ink-receptive areas of the printing plate, the additive must remain uniformly dispersed throughout without agglomerating in localized areas, thereby causing faulty impressions. Also, the colloidal character of the organic coated silica particles is necessary in order that the rheological properties of the planographic ink such as viscosity, flow, consistency, electrical attractions and repulsions, surface tensions, interfacial tensions, wetting forces, etc., are not deleteriously affected.

The additive organo-coated silica particles of the invention, all dispersible in organic hydrophobic media, are known materials which are normally prepared by first forming an aqueous silica sol containing small particle size

silica such as through the process described in Bird United States Patent 2,244,325. These sols are then concentrated by known means such as that set forth in the Bechtold and Snyder United States Patent 2,574,902 and Reuter United States Patent 2,929,790. These aqueous sols are in turn converted into organo sols to which are added a variety of reactive agents and most preferably higher aliphatic alcohols capable of esterifying the silica particles through reaction of the surface silanol groups. There is then formed by the reaction an organic coating around the core of the silica particle so as to impart thereto a hydrophobic character. These reactions are accomplished in such a manner that substantially little gelation or agglomeration of the individual colloidal silica particles takes place.

As mentioned above, the preferred organic coated silica particles of the invention are those formed by esterification of aliphatic alcohols. Monohydric alcohols are preferred as the surface-esterifying agent and among these may be chosen n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-dodecyl, etc. Branch chain primary alcohols may also be employed such as isoamyl, isobutyl, etc.

Alicyclic alcohols such as cyclopentanol, and menthol, etc., as well as ethylenically unsaturated alcohols such as allyl and crotyl may also be used. Acetylenic unsaturated alcohols typified by propargyl alcohol are also useful reactants. Mixtures of any of the above may likewise be used.

Preferred alcohols which may be used as esterifying agents are those containing from 2 to 22 carbon atoms and are monohydric in chemical constitution. More preferably, the alcohol contains from 6 to 16 carbon atoms. Saturated or unsaturated, branched or linear types may be employed.

One excellent source of alcohols which may be used as the surface-esterifying agent is that class known as oxo alcohols. These are normally a mixture of various intermediate molecular weight alcohols ranging from 6 to about 16 carbon atoms. Their preparation and description is described in the book "Higher Oxo Alcohols," by L. F. Hatch, Enjay Company Incorporated, 1957, which disclosure is herein incorporated by reference. A typical oxo alcohol which has found excellent use in preparing the organic coated silica particles involved in the invention has the following composition.

Alcohol:	Percent
Octyl -----	5
Nonyl -----	10
Decyl and higher -----	35
Impurities (esters, soaps, etc.) -----	50

Suitable organo coated silicas for use in the invention and their methods of preparation are found in United States Patent 2,801,185 and in copending application, Serial No. 254,417, filed January 28, 1963.

Planographic inks are well-known in the art, and are distinguishable as all being hydrophobic in nature. Therefore, the organic coated silica additives of the invention may be suitably incorporated into almost any of these commercial inks. These inks are generally composed of vehicles such as vegetable drying oils, linseed oil and linseed oil varnishes, lithographic varnishes (linseed oil bodied by heat), tung oils, soybean oils, cottonseed and rapeseed oils, pitch varnishes, rosin oils, alkyl oils, epoxy vehicles, etc.; and natural, manufactured, or organic pigments such as barytes, china clay, ochres, venetian red, calcium carbonate, blanc fixe, aluminum hydrate, chrome green, titanium dioxide, vermilion, white lead, alizarine madder lake, benzidine yellow, brilliant lake, ethyl violet, pigment scarlet, etc. In addition, the planographic ink generally contains a drier such as a cobalt drier, amine accelerator, paste drier, etc. Other constituents may include solvents such as ketones, alcohols, esters, ethers, hydrocarbons, etc., as well as modifiers to improve the working and setting qualities of the ink and eliminate troubles of offsetting, sticking and picking. These may

include greases, tallow, beeswax, vegetable waxes, anti-oxidants, wetting agents, deodorants and reodorants, etc.

As seen above, the ingredients of the planographic ink generally comprise a vehicle made up of either oils or varnishes, pigments and driers. These ingredients as well as the amount of organic coated silica additive may be varied over a wide range. In high speed printing operations solvents are frequently added to the ink to reduce viscosity. The following general formula may be considered as typical, showing ranges of the various constituents.

Formula I

Ingredient:	Amount, parts
Vehicle -----	10-90
Pigment -----	10-90
Drier -----	1-15
Silica additive -----	1-20

Typical planographic inks including the silica additive may be made up according to the following:

Formula II

Ingredient:	Amount, parts
Lithographic varnish -----	33
Paste drier -----	2
Cobalt drier -----	1
Gloss white -----	26
Permanent blue toner -----	26
Organo-coated silica -----	2

Formula III

Ingredient:	Amount, parts
#3 Lithographic varnish -----	23
Alkali reflex blue paste -----	11
Cobalt drier -----	1.6
Oil drier -----	3.6
Carbon black -----	10.5
Organo-coated silica -----	4.8

Formula IV

Ingredient:	Amount, parts
Titanium dioxide -----	32
Aluminum hydrate -----	4.8
Long Oil alkyd resin -----	33.8
Cobalt linoleate drier, 3% metal -----	.8
Organo-coated silica -----	2.7
Kerosene -----	40.0

Formula V

Ingredients:	Amount, parts
#3 Lithographic varnish -----	57
#5 Lithographic varnish -----	3.2
Cobalt drier -----	3.9
Non-bleeding peacock blue -----	40.0
Zinc oxide white -----	38.8
Organic coated silica -----	6.7

The above are merely illustrative of the type of planographic inks which may be incorporated with the silica additives of the invention resulting in ink compositions having improved properties. It is understood, of course, that the invention is not limited to the specific embodiments but rather lies in the fact that any type of planographic ink, that is, an ink employed in a planographic process such as stone lithography, offset lithography, dry offset printing, offset tin printing, heat-set web offset, etc., may be improved by the silica addition.

In order to benefit the planographic ink, it is only necessary to add the organic coated silica material which may either be in a dry form or as an organosol, either to one of the individual constituents of the planographic ink or to the ink itself after it has been composed. One preferred method is to incorporate the organic coated silica as it exists in solid form, into the same ink vehicle as that used to make up the planographic ink itself. This

solution or dispersion of vehicle and organic coated silica particles is then incorporated into the planographic ink. For best results, from 1 to 20% by weight of coated silica particles based on the weight of the ink are added to the planographic ink material.

In order to test the effectiveness of a typical organic silica additive the following material was prepared. To a typical silica organosol was added an oxo alcohol and the resultant mixture was heated at high temperatures to effect esterification. At the end of the reaction it was calculated that over 90% of the silanol groups on the colloidal silica particles which were available for surface reaction were esterified with the oxo alcohol, giving an extremely hydrophobic substance. The oxo alcohol esterified silica particles were first incorporated into a long oil alkyd resin, which combination was in turn added to an offset Milori Blue planographic ink. Sufficient silica was compounded into the resin so that the final treated ink composition contained 3% by weight of silica additives.

The above ink had been previously employed without benefit of any additive in a heat-set web offset process and specifically one of the blanket-to-blanket design or prefector press type. In such a printing process, there are no impression cylinders, but rather the blanket cylinders of one unit become the impression cylinder for the opposing unit. The untreated blue planographic ink emulsified between about 15 and 20% of water based on the weight of ink after use of approximately 4-8 hours. This emulsification resulted in the fact that the ink became much more viscous, and thereby necessarily lowered the speed of the operation. Again, since the operational speed had to be adjusted, the chance for emulsification increased and the problem became compounded by further viscosity increase. The emulsification resulted in changes in color intensity, and many variances in rheological properties of ink. In addition the drying characteristics or heat-set properties were also deleteriously affected. Specifically, the ink drying time was increased due to reaction of the emulsified water with the drier. Also, the color itself was somewhat diluted and did not give a sharp, clear and true color impression. In view of all of these undesirable characteristics of the ink, the operation had to be shutdown and fresh ink supplied to the process after equipment cleaning.

A quantity of the silica-treated blue planographic ink was then used in the offset printing process for comparative purposes. After many hours of use, substantially no emulsification of water into the ink was noted. And, in fact, after many days' service, the process was still running smoothly with no machine downtime. Specifically, no ink was wasted, and any excess ink caught during the process could be recirculated without fear of improper effect. The ink remained in an excellent consistency approximating that when formed. There were substantially few rejects of paper, and the ink maintained its proper imprint upon the paper, producing an excellent impression of proper color and intensity. The silica particles maintained the delicate hydrophobic-hydrophilic balance necessary for sharp and intense impressions. No tendency of the water or ink to crawl on the plate causing disappearance of image was noted, even though the silica particles are themselves highly hydrophobic, and necessarily imparted some measure of hydrophobicity to the ink itself. The viscosity of the ink was maintained as originally formulated, thus allowing the relatively high speed operation to continue in a safe and efficient manner. Also, the drying characteristics of the planographic ink were not altered to any substantial degree, and proper rapid drying was maintained.

The exact theory as to how the hydrophobic silica particles prevent water in ink emulsification and keep the ink in its proper original form along with the other above specified advantages is not exactly known. It is specu-

lated that minor amounts of surface active agents are extracted from paper during the planographic process and gradually become incorporated into both the ink and water fountains. This, in turn, causes an increase in emulsification and a lowering of surface tension as the surface active agents become more and more concentrated upon continued planographic operation. It is further hypothesized that the silica particles due to their large surface area are able to adsorb or absorb these surface active agents and thereby prevent emulsification of the planographic ink and water. The proper ink consistency is thus maintained by the silica additive without altering any of the desired rheological properties of the ink.

The invention is hereby claimed as follows:

1. An improved planographic ink composition useful in lithographic and offset printing processes which comprises a major portion of a planographic ink and 1-20% by weight of said ink of organo dispersible silica particles having average diameters of from about 5 to about 150 millimicrons and having chemically bound organic hydrophobic surface coatings, said composition being further characterized as having substantially no tendency to emulsify in the presence of aqueous solutions.

2. The ink composition of claim 1 wherein said silica particles are surface-esterified with a monohydric alcohol containing from 2 to 22 carbon atoms.

3. The composition of claim 1 wherein said silica particles are surface-esterified with a monohydric alcohol containing from 6 to 16 carbon atoms.

4. The ink composition of claim 1 wherein said silica

particles are surface-esterified with a mixture of monohydric alcohols containing from 6 to 16 carbon atoms.

5. In a planographic process which comprises the steps of preparing a slightly etched plane surface having both ink receptive and ink repellant areas, treating said surface with an aqueous liquid and a planographic ink, and contacting said treated surface with a paper sheet whereby an inked impression is made thereon; the improvement which comprises treating said planographic ink with 1-20% by weight of said ink of organo-dispersible silica particles having an average diameter of from about 5 to about 150 millimicrons and having a chemically bound organic hydrophobic surface coating, whereby emulsification of said ink and said aqueous liquid is substantially prevented, and said inked impression is produced in a sharply defined condition.

6. The method of claim 5 wherein said silica particles are surface-esterified with a monohydric alcohol containing from 2 to 22 carbon atoms.

7. The process of claim 5 wherein said silica particles are surface-esterified with a monohydric alcohol containing from 6 to 16 carbon atoms.

8. The method of claim 6 wherein said silica particles are surface-esterified with a mixture of monohydric alcohols containing from 6 to 16 carbon atoms.

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