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SURFACE USEFUL MATERIALS

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This invention relates to planographic printing and more particularly to improvements in planographic printing plates.

The functioning of a lithographic printing plate is ordinarily dependent on the presence of a grease-receptive printing area adapted to retain the lithographic ink, and a water-receptive, grease-resistant, non-printing area adapted to resist retention of the lithographic ink. The use of certain types of polyvinyl alcohols, for both the printing and non-printing areas in the preparation of planographic printing plates, is disclosed in, inter alia, U. S. 2,230,982, U. S. 2,302,817, and U. S. 2,302,816. However, from a practical standpoint, the use of polyvinyl alcohol in the preparation of planographic printing plates is not entirely satisfactory without the addition of fillers or further hardening treatments since available polyvinyl alcohols are somewhat too water-sensitive, that is, they swell too much in the presence of water, are too soft, and have a tendency to break away from the back support.

An object of this invention is the preparation of improved planographic printing plates. A further object is to provide a planographic printing plate in which the grease-resistant areas comprise a hydrophilic resin of improved properties. Further objects will appear hereinafter.

These objects are accomplished by a lithographic printing plate in which the grease-resistant, water-receptive, non-printing areas comprise an essentially completely hydrolyzed ethylene/vinyl acetate copolymer, containing after hydrolysis from about 3 to 30% by weight of ethylene. These hydrolyzed ethylene/vinyl acetate copolymers, after suitable treatment with a water-soluble light-sensitive bichromate, exposure to light, and development, can also be satisfactorily employed in the grease-receptive printing areas of the lithographic plate.

In the usual method for preparing a lithographic printing plate using these new materials a dilute aqueous solution (2–10%) of the hydrolyzed ethylene/vinyl acetate copolymer is coated on a suitable support, for example, metal, glass, plastic, or paper, and permitted to dry. The coating is then sensitized to light by treatment with an aqueous solution of a light-sensitive bichromate and dried. The dried film is then suitably exposed to light through a negative and the exposed places developed by coating with lithographic developing ink or a suitable vegetable oil, for example, linseed oil. The oil coating is removed from the grease resistant areas by rubbing gently with a pad of soft fibrous material moistened with water or aqueous gum arabic solution, which leaves the light-exposed areas grease receptive and the unexposed areas grease-resistant. After this treatment, the plate is then ready for printing and may be inked in the usual manner with regular lithographic ink, and used as a lithographic plate.

The hydrolyzed ethylene/vinyl acetate copolymers used in coating these lithographic printing plates are prepared in accordance with the process described in Roland S. N. 446,114 filed June 6, 1942, a continuation-in-part of which issued October 9, 1945, as U. S. Patent 2,386,347. Hydrolyzed ethylene/vinyl acetate copolymers falling within the above mentioned limits are all film-forming materials which are water-sensitive in varying degrees depending on the ethylene content and which are capable of forming grease-resistant surfaces and, after suitable treatment herein described, grease-receptive or lithographic ink-receptive surfaces.

The more detailed practice of the invention is illustrated by the following example, wherein parts given are by weight. There are, of course, many forms of the invention other than this specific embodiment.

Example

A hydrolyzed copolymer of ethylene and vinyl acetate is prepared as described in Example 11 of Roland Serial No. 446,114, filed June 6, 1942.

A 5% aqueous solution of the above copolymer is acidified with a few drops of hydrochloric acid and spread on a glass plate. The film is allowed to dry at room temperature and is then bathed with a 5% aqueous solution of ammonium dichromate and dried in the absence of light. This light-sensitive film is then exposed behind a line negative to a mercury arc lamp (Mazda H–4) for ten minutes at a distance of 15 inches from the source of the light. The exposed plate is coated with linseed oil and is then rubbed gently with a cotton pad which has been moistened with aqueous gum arabic solution. The gum arabic solution swells the unexposed portions of the film and removes the oil film but does not affect the exposed areas of the film. The developed and moistened plate is then coated with a lithographic ink which adheres to the exposed portions, but is repelled by the moisture-swollen unexposed areas. Thus, when the ink image is transferred to paper or other printing surfaces, a positive image of the original negative results.

The hydrolyzed ethylene/vinyl acetate polymers useful in this invention are those in which the hydrolysis is essentially complete, that is, those in which at least 95% of the acetate groups have been hydrolyzed to hydroxyl groups. The hydrolyzed polymers contain at least 3% ethylene by weight and not more than 30% ethylene by weight, the remainder comprising essentially hydrolyzed polyvinyl acetate. The polymers containing less than 3% ethylene are too water-soluble to function satisfactorily on a lithographic plate and tend to wash off the plate with the

water or gum arabic solution applied after development. Polymers containing more than 30% of ethylene by weight are insufficiently water-sensitive and do not have satisfactory grease-repellent characteristics for use in the non-printing areas of the lithographic plate. Because of their excellent hydrophilic and grease-resistant properties, polymers having from four to 10% of ethylene are preferred.

The hydrolyzed ethylene/vinyl acetate copolymers, i. e., the polyvinyl alcohol-ethylene copolymers, can be coated on any suitable base material, for example, metals, plastics, paper, wood or glass which is adapted as a support for a printing plate.

If desired, the light-sensitizing material, for example, ammonium dichromate may be mixed directly with the hydrolyzed ethylene/vinyl acetate copolymers and coated on the support. Since these copolymers are not soluble in cold water, after exposure the ammonium bichromate can be washed out of the unexposed portions by water.

If desired, a planographic lithographic plate can also be prepared by first coating the support with the hydrolyzed ethylene/vinyl acetate copolymers and subsequently applying a coating of dichromated albumin solution, exposing to light to harden the albumin in the exposed areas, developing and washing to remove the unhardened areas of albumin. The hydrolyzed ethylene/vinyl acetate copolymer film remaining on the plate may then be used as the water-receptive, grease-resistant base in the non-printing areas. Likewise a lithographic plate may first be prepared in the normal manner from bichromated albumin or similar colloid, and, after development with ink and moistening of the non-printing areas with water, an aqueous solution of hydrolyzed ethylene/vinyl acetate copolymer is applied to coat the non-printing areas of the plate.

Other light-sensitive colloidal materials may be coated over the hydrolyzed ethylene/vinyl acetate copolymers. For example, a gelatin emulsion containing a silver halide salt such as silver bromide can be coated over the hydrolyzed ethylene/vinyl acetate in the absence of light. The plate is then suitably exposed to light and the latent image silver salt developed with a developer such as hydroquinone and fixed with a suitable fixing agent. The resulting silver image in gelatin is thereafter converted by treatment with ammonium bichromate to silver chromate. The colloid containing the unexposed light-sensitive salt is finally washed away in warm water leaving the photographic image in the hardened gelatin and anchored to the hydrophilic base. By coating a suitable base with a silver halide emulsion prepared in a solution of hydrolyzed ethylene/vinyl acetate copolymer, the above described process can be carried out without use of gelatin, i. e., the printing area is the hardened hydrolyzed ethylene/vinyl acetate copolymer furnished by bichromate treatment of the silver image in the hydrolyzed ethylene/vinyl acetate copolymer.

Although fillers such as clay or water-insensitive resins may be employed with the hydrolyzed ethlene/vinyl acetate copolymers, this is not necessary since the copolymers are insoluble in water at room temperature and remain on the plate during the washing operation. These hydrolyzed ethylene/vinyl acetate copolymers have definite advantages over materials formerly used for presenting a grease-repellent surface since they have excellent wet film strength and a reduced swelling tendency in water as shown by the following table.

	Tensile strength after 24 hrs. in water at 25° C.	Linear swelling after 30 min. in water at 30° C.
	Lbs./sq. in.	*Per cent*
Hydrolyzed ethylene/vinyl acetate copolymer (3–30% ethylene)	1,500–5,000	3–40
Commercial high viscosity completely hydrolyzed polyvinyl alcohol	Less than 400	70

At the same time they maintain sufficient water-sensitivity to provide, after moistening, the necessary grease-repellent surface. These materials make possible line, continuous or half-tone printing and permit the use of fine half-tone screens because no fillers are present. The plates can be used in direct and offset planographic printing. The higher wet tensile strength is of great practical advantage in that they have greatly reduced tendency to damage on the press in comparison with hydrophilic materials previously used. Furthermore, the printing plates of this invention permit longer printing runs with one plate and give sharp clean printing, and moistening is less critical to maintain the hydrophilic character of the non-printing areas.

Photographic elements comprising hydrolyzed vinyl acetate-ethylene copolymers and light-sensitive materials, e. g., silver halides, are disclosed and claimed in the copending application of D. M. McQueen, Serial No. 528,945, filed March 31, 1944.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included in the scope of the claims.

What is claimed is:

1. An improved process of making a planographic printing plate which comprises providing a suitable base, coating said base with a substantially completely, hydrolyzed vinyl acetate-ethylene polymer having, after hydrolysis, from 3–30% ethylene in the copolymer and selectively locating grease-receptive printing layers on the interpolymer surface.

2. An improved process of making a planographic printing plate which comprises providing a suitable base, coating said base with a vinyl alcohol-ethylene copolymer having from 3–30% ethylene in the interpolymer and selectively locating grease-receptive printing layers on said copolymer coatings.

3. As an article of manufacture a planographic printing plate comprising printing portions and non-printing portions, said printing portions comprising a vinyl alcohol-ethylene copolymer of from 3–30% ethylene content, said copolymer being hardened with a light-sensitive salt.

4. A continuous tone printing plate comprising a base material having a coating which comprises a vinyl alcohol-ethylene copolymer of from 3–30% ethylene content, selected areas only of said coating being relatively harder than other areas and being grease-receptive, the other areas being water-receptive.

5. A planographic printing plate comprising printing portions and non-printing portions, said printing portions consisting essentially of a vinyl alcohol-ethylene copolymer of 3–30% ethylene content.

6. A plate for planographic printing comprising a suitable base coated with a vinyl alcohol-ethylene copolymer of 3–30% ethylene content sensitized with a light-sensitive chromate.

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