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[54] **ELECTROPHOTOGRAPHIC LIQUID DEVELOPER CONTAINING ASPHALT AND MODIFIED ALKYL RESIN**

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[58] **Field of Search** 252/62.1

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[57] **ABSTRACT**

An electrophotographic liquid developer is provided which comprises a dispersion of at least one coloring material in particle form, asphalt and synthetic resin in an organic solvent having an electrical resistance of no less than $10^8\Omega$. The liquid developer is useful for the preparation of lithographic plates.

4 Claims, No Drawings

ELECTROPHOTOGRAPHIC LIQUID DEVELOPER CONTAINING ASPHALT AND MODIFIED ALKYL RESIN

This invention relates to an electrophotgraphic liquid developer, particularly available for the preparation of lithographic plates.

Heretofore, a liquid developers in electrophotography has only been contrived for mainly applying them to electrostatic copies and accordingly, has never been employed in the preparation of so-called "lithographic plate" by which a large number of printed matter whereon highly images are printed, is produced. Because, in the case when conventional liquid developer is employed in the process of preparing the lithographic plate, the following defects are produced; first, a deposited amount of toner constituting images on an electrophotosensitive paper is less and in many cases, due to so-called "fringing field effect" peculiar to a dry-type electrophotographic process, the serious loss of image density in the central part of half-tone images or of the solid area whereon toner should be wholly deposited is caused. Secondly, the weak adhesive power of toner particles to the lithographic plates results in poor receptivity of printing ink and in diminution of images on printing because the printed images cannot withstand the roller pressure produced at the time printing.

Generally, in order to obtain good images on a lithographic plate, toner particles should have characteristics which satisfy the following prerequisites;

1. Toner particles should carry a stable positive charge.
2. They should have a microscopic fineness and electrical characteristics exhibiting high resolving power.
3. They should be superior in fixation property so that diminution of the printed images may be prevented.
4. They should exhibit good receptivity of printing ink.
5. They should have good abrasion resistance.
6. They should cause less fog formation on the unexposed area.
7. The fringing field effect should appear least and accordingly, good tone reproduction of the photograph or of the solid area whereon toner particles should completely be deposited, is obtainable.

The object of the present invention is to obviate the above-mentioned defects present in the conventional lithographic processes and accordingly, to provide an electrophotographic liquid developer useful for the preparation of lithographic plates which have the characteristics satisfying the above-listed prerequisites.

According to the present invention, there is provided an electrophotographic liquid developer useful for the preparation of lithographic plates, comprising a uniform dispersion of at least one coloring material (pigment or dyestuff) in particle form asphalt and synthetic resin, selected from petroleum resin and oil modified synthetic resin in an organic solvent having an electrical resistance of no less than $10^8\Omega$cm, said synthetic resin being at least partially soluble in the organic solvent.

The coloring material (dyestuff or pigment) which is used in the liquid developer of the present invention includes not only carbon black, but also those of various hues, for example, Phthalocyanine Blue, Chrome Yellow, Aniline Black, red iron oxide Oil Black, Oil Red and Malachite Green because the developer has various uses other than copying. As dyestuffs, those which are insoluble in a dispersion medium, that is, the organic solvent, are preferable. The particle diameter of the colorant used in the liquid developer is preferably no more than 10 μ because microscopic particles produce a lithographic plate having a higher resolving power.

The asphalt which is contained in the liquid developer usually comprises asphaltene, maltene and oily ingredients.

The synthetic resin which is used in the liquid developer should be at least partially soluble in the organic solvent mentioned later. Useful synthetic resin of this class includes resin and petroleum resin, oil-modified synthetic resin.

The organic solvents which are used in the liquid developer are those having an electrical resistance of no less than $10^8\Omega$cm, for example, solvent naphtha, mineral turpentine, turpentine oil, kerosine, n-heptane, carbon tetrachloride, etc. In case the composition of coloring material, asphalt and synthetic resin is previously mixed using a mixer such as a ball mill, it is preferable to employ an organic solvent containing aromatic hydrocarbon having high dissolving power, for example, solvent naphtha, mineral turpentine or turpentine oil.

The content of the coloring material may vary within a range from 5 to 75 percent by weight based on the total solid content in the liquid developer depending upon the particular coloring material and its physical and chemical properties the remaining solid material, i.e. asphat and resin, are than present in an amount of 95 to 25 percent by weight.

The content of asphalt also depends upon the particular asphalt and its characteristics and may vary within a range from 1 to 90 percent by weight based on the total solid content other than pigment. However, the content of asphalt has relevance to the receptivity of ink and, in view of the characteristics required as line images on lithographic plate, it is preferable to employ from 1 to 10 percent by weight of asphalt based on the total solid content. Further, the content of the synthetic resin may also vary within a range from 10 to 99 percent by weight based on the total solid content other than pigment depending upon its ratio to the content of asphalt.

The effects and functions exercised by the above three ingredients in the liquid developer will be described hereinafter.

The coloring material particles function as image-forming elements in the developer. In view of the fact that the liquid developer of the present invention is available for uses other than the usual copying, the developer can be made in any color; the coloring material may include those of various hues besides carbon black. It is, however, noted that content of both asphalt and synthetic resin should be determined in dependence of the particular coloring material because coloring materials usually have quite different physical and chemical properties from each other. For example, in the case of the coloring material having a higher oil absorption, the content of both asphalt and synthetic resin may be increased. On the other hand, if the color-

ing material has little oil absorption, the content of the asphalt and synthetic resin should be decreased.

Asphalt is in a massive state composed of associated micelles. It comprises asphaltene, maltene and oily materials. It is easily soluble in organic solvent mainly containing aromatic hydrocarbon having a high dissolving power, i.e., solvent naphtha, mineral spirit, terpentine oil and the like. Some organic solvents having a high electrical resistance which are usually available as diluent, have a lower dissolving power and therefore, they do not completely dissolve asphalt. However, even in that case, asphalt forms fine colloidal particles having a high polarity and consequently, exhibits high adsorption together with asphalt micelles dissolved in the organic solvent. Consequently, the asphalt is adsorbed on the coloring material particles so that charged colloidal particles composed of coloring material and asphalt are formed. The colloidal particles carry positive charges and thusly are repelled by each other by like charges to produce stable image-forming particles.

Synthetic resin is dissolved in the organic solvent to form a stable organosol and the organosol is adsorbed as a protective colloid with respect to the above-mentioned colloidal particle comprising coloring material and asphalt to form stable colloidal particles comprising coloring material, asphalt and the synthetic resin.

Some coloring material and the synthetic resin have little wetting property or low oil absorption and therefore, the mixture of the coloring material and the synthetic resin has a tendency to give an unsatisfactory fixation of developed images. But in practice, as asphalt is extremely adsorbent on the coloring material, stable colloidal particles comprising coloring material, asphalt and the synthetic resin are also obtainable. Thusly formed colloidal particles carrying charges, go hand in hand with protective colloidal action by synthetic resin to prevent the developing agent from aggregating. In other words, because asphaltene micelles composing asphalt are extremely adsorbent and carry high positive charges, the colloidal particles of coloring material-asphalt-synthetic resin carry positive charges in the aggregate and consequently prevent aggregate-formation between particles.

In view of the fact that the purposes of the synthetic resin used in the present invention includes the exertion of a protective colloidal action on the coloring material-asphalt colloidal particles and the achievement of a satisfactory fixation of developed images, the synthetic resin need not function as a polarity-controller. Accordingly, the synthetic resin used in the present invention may be chosen from those which are at least partially soluble and stably dispersible in organic solvent having an electrical resistance of no less than $10^8\Omega$cm and which do not reduce the electrical resistance of the organic solvent to that which is less than $10^8\Omega$cm. Further, it will be noted that toner particles containing the synthetic resin should be easily solidified by evaporation of organic solvent from the toner particles constituting just developed images or should be spontaneously solidified through oxidative polymerization of the synthetic resin contained in the toner particles.

One of the most noticeable aspects of the present invention is that absence of any one component of the above-mentioned coloring material-asphalt-synthetic resin never answers the purpose of the present invention, that is, satisfactory line images on lithographic plate cannot be obtained. For example, in case the developing solution containing only coloring material-asphalt colloidal particles and not containing the synthetic resin is employed, line images so formed are easily destroyed by the roller pressure applied in printing, not to mention mechanical action exerted in development and consequently, they stain the background because physical adsorptive power (fixation) of the toner particles and frictional resistance are extremely low. On the other hand, in the case of a developing solution containing only coloring material-synthetic resin particles, good images cannot be obtained or, even if better formation of the highly resolved images is expected, as the adsorptive power of the synthetic resin in the coloring material is inferior to asphalt, line images thusly formed are lacking in receptivity of printing ink. Furthermore, in the case of a developing solution containing only asphalt-synthetic resin colloidal particles, as no image-forming elements exist the deposited amount of toner on a charged area, on which line images are to be formed, is reduced. Therefore, the above three developers are not suitable for a printing plate.

On the contrary, the developer of the present invention containing the above three components, obviates the above defects and accordingly, it exhibits excellent stability, good fixation and high resolving power. It also exhibits superior reproducibility of all kinds of images such as solid, half tone or thin line and produces good receptiveness of printing ink.

The following examples will serve to illustrate the present invention, in which all parts are by weight.

EXAMPLE 1

The following composition, which contained
10 parts of carbon black,
5 parts of blown asphalt having a hardness scale (penetration of the indentor) of 50 – 60,
50 parts of long soybean oil (50 percent)-alkyd resin; and
35 parts of kerosine
was dispersed for 20 hours in a ball mill and then, the resultant dispersion was diluted with 20 l of kerosine to obtain a developing solution. Using the developing solution, an image was formed on a master paper on which an electrophotosensitive layer was coated. The resultant lithographic plate was set up on an offset printing machine after the image-undeveloped area of the printing plate surface was desensitized to oil. 1,000 sheets of printing matter were printed by the offset machine. Various kinds of printed images, such as photography, large solid area or thin line were extremely clear.

EXAMPLE 2

The following composition, which contained
15 parts of Phthalocyanine Blue,
10 parts of Oil Black,
5 parts of blown asphalt having a hardness scale (penetration of the indentor) of 30 – 40,
40 parts of vinyltoluene oil containing 40 percent of vinyltoluene; and
30 parts of n-heptane

was mixed and dispersed for 20 hours in a ball mill and then, the resultant dispersion was charged into 30 l of n-heptane with stirring to obtain a developing solution. Using the developing solution, a lithographic plate was prepared and 5,000 sheets of printing matter were printed in the same manner as described in Example 1. Various kinds of printed images, such as photography, large solid area or thin line exhibited good tone reproduction and excellent clearness.

EXAMPLE 3

A following composition, which contained
20 parts of Malachite Green,
10 parts of straight asphalt having a hardness scale (penetration of the indentor) of 100 – 120,
40 parts of terpene resin; and
30 parts of carbon tetrachloride
was mixed and dispersed in a ball mill for 15 hours and then, the resultant dispersion was diluted with 20 l of kerosine to obtain a developing solution. Using the developing solution, lithographic plates were prepared and 3,000 sheets or printing matter were printed as described in the above Examples. The printed images were clear as described above.

What we claim is:

1. An electrophotographic liquid developer for the preparation of lithographic plates which comprises a uniform dispersion of at least one coloring material in particle form having an average particle diameter of no more than 10 microns selected from pigment and dyestuff capable of carrying a positive charge, asphalt and an oil modified alkyd resin, in an organic solvent having an electrical resistance of no less than $10^8\Omega$ cm., said resin being at least partially soluble and not reducing the electrical resistance of said solvent to less than $10^8\Omega$ cm., said dispersion containing 5 to 75 percent by weight of said coloring material based on the total weight of solid material and in the remaining solid material of said dispersion, said oil-modified alkyd resin being present in an amount of 10 to 99 percent by weight and said asphalt in an amount of 1 to 90 percent by weight based on the amount of said asphalt and resin in said dispersion.

2. An electrophotographic liquid developer according to claim 1 wherein said coloring material is insoluble in said organic solvent.

3. An electrophotographic liquid developer according to claim 1 in which said organic solvent contains aromatic hydrocarbon.

4. An electrophotographic liquid developer according to claim 1 in which said oil-modified alkyd resin is a soybean oil-alkyd resin.

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