A process for bleaching an electrophotographic photosensitive layer having an image thereon, the image containing a lake pigment soluble in an acid to obtain an improved color print which comprises treating at room temperature the colored electrophotographic photosensitive layer composed of a dispersion comprising zinc oxide, resinous binder and a dye selected from the group consisting of triphenylmethane and xanthene dyes and pdimethylaminobenzylidene rodanine with a bleaching solution containing (I) 30 to 80% by weight of a solvent for the day, (II) 0.01 to 20% by weight of an alkali hydroxide and at least one of (III) less than 10% by weight of an organic solvent capable of dissolving or slightly swelling the resinous binder and (IV) a cationic active agent thereby changing the photosensitive layer substantially white, and then washing the thus treated layer with a washing liquid comprising at least one of the components (I) and (III) or with the washing liquid added with acid.

15 Claims, No Drawings
This invention relates to a process for bleaching substantially the coloration of electrophotographic photosensitive layer caused by dye material added to electrophotographic photosensitive layer comprising zinc oxide in order to sensitize said zinc oxide or to modify the color of said photosensitive layer.

The photosensitive layer usually comprises a dispersion of zinc oxide in a resinous binder, such as a polyvinyl resin, e.g., polystyrene, polyvinylacetate, polyvinyl chloride, etc., and copolymers of these, the silicone resins, cellulose esters and cellulose ethers, and the acrylic resins, e.g., the poly(methacrylates), the poly(methyl methacrylates), etc. These resins are hydrophobic and must have good electrical insulating properties. Various optical sensitizers are used to extend the optical sensitivity of the zinc oxide. These include triphenylmethane dyes, such as Rose Bengal, Fluorescein, Crystal Violet, etc., ketonine dyes, such as Auramine B, etc., xanthene dyes, such as Rhodamine B, etc.

Addition of dye to electrophotographic photosensitive layer using zinc oxide principally has the purpose of spectral sensitization of zinc oxide, as already stated above and reported in various references and patents. In certain dyes it is reported that an addition amount of 0.03 to 0.05% with respect to the weight of zinc oxide gives rise to an optimum result. This result, however, cannot be applied to every case. Apart from the efficiency of sensitization, the photographic sensitivity becomes higher as the amount of dye increases. Thus the whiteness and photosensitivity of photosensitive layer are contradicting each other, and higher sensitive layer realized by dye sensitization usually accompanies elevated coloration. Such coloration should naturally be restricted as small as possible in order to obtain the reproduced image of better quality, and it becomes consequently necessary to effect bleaching operation in case of highly sensitive layer.

The coloration of photosensitive layer can be decreased by exposing said layer in a lighted place for a prolonged period because of relatively inferior light fastness of sensitizing dye usually employed in the photosensitive layer. The fairly dense coloration in highly sensitive layer requires, however, extremely long period for realizing appropriate bleaching. Also the layer thus bleached has a drawback of retaining yellowish hue due to decomposition product resulting from sensitizing dye. Besides, apart from the drawbacks connected directly with dye, the prolonged exposure to light is impractical since this will lead to deterioration of mechanical properties of photosensitive layer itself and to fading of obtained image.

On the other hand chemical bleaching using solution of organic acid such as oxalic or maleic acid is reported in U.S. Pat. No. 3,250,614. This method accompanies an important drawback of bleaching the obtained image also if lake pigment susceptible to acid such as Brilliant carmine 6B is used in toner.

The purpose of this invention is to provide a novel process for bleaching electrophotographic photosensitive layer containing dye.

Another purpose of this invention is to provide a bleaching process particularly effective for electropho-
component (III). Also it will be readily understandable that the bleaching bath of this invention is far superior to the conventional acidic bleaching solution, as the former does not affect toner image containing lake pigment and furthermore shows greater speed.

Also it is experimentally confirmed that the bleaching process of this invention is particularly effective in photosensitive layer in which zinc oxide is sufficiently dispersed in resinous binder.

The components constituting the bleaching bath of this invention will be discussed detailedly in the following.

The component (I) is added in order to dissolve the dye contained in the sensitive layer, and should preferably contain a small amount of acetone, presumably because acetone not only dissolves dyes but also performs the function of component (III), namely of accelerating bleaching. The selection of components (I) and (III) should be cautiously carried out so as that they do not deteriorate the sensitive layer nor the image formed thereon. As is explained in the following, the amount of solvent for the resinous binder should preferably be less than 10 wt.% in bleaching bath when the resinous binder is not cross linked, although the photosensitive layer itself is not attacked in the course of bleaching even if the components (I) and (III) are composed of abundant amount of highly capable solvents such as ketones, esters, cellosolve, aromatic hydrocarbons or chlorinated hydrocarbons, if the resinous binder in the photosensitive layer is crosslinked and thus is hardly soluble against most solvents.

Resinous binder in cured state facilitates bleaching procedure and enables the use of simple mechanical operation in removing bleaching solution from the surface of photosensitive layer, such as mechanical squeezing.

Among the members cited in the group (1), sufficient caution should be paid to water, of which presence may lead to enhancement of the action of alkali hydroxide against photosensitive layer and various dyes. Thus the concentration of water should preferably be maintained within a certain limit according to the species of the dyes used. An effective method consists of adding a substance which is insoluble in the bleaching bath and which absorbs water, such as Molecular sieve (Linde Corp., U.S.A.), Silica gel or alumina gel. In this way, the incorporation of water vapor into the bleaching bath caused by the evaporation of volatile components in said bath cannot result in any undesirable effect.

In general, the concentration of water in bleaching bath should preferably be less than 10 wt.% when lake pigment is contained in toner. The component (I), which at the same time works as the solvent for alkali hydroxide, is generally employed in an amount of 30 to 80 wt.% in the bleaching bath. Among the members cited before, methanol and ethanol do not show the function of swelling the resinous binder, whereas acetone performs a function as the component (III). When the resinous binder is composed of polyvinyl acetate which is relatively soluble in methanol, the concentration thereof should be decreased since, in this case, methanol works also as the component (III).

The component (III) can be employed in an elevated concentration when the binder is crosslinked. Otherwise, the solvent for binder should be removed or should be less than 10 wt.%. The bleaching treatment can be accelerated at an elevated temperature, but in this case sufficient caution is required since the influence of the component (II) becomes stronger.

The species of resin component of toner and solubility thereof in bleaching bath has been excluded from the foregoing discussion, but it is proved unavoidable that the mechanical strength of toner image is deteriorated by a bleaching bath capable of dissolving resin component in the toner. This drawback can be prevented by using strongly polar composition in the bleaching solution (such as that chiefly composed of methanol, ethanol and acetone) and employing resin insoluble in these solvents. Although most resins are soluble in acetone in common sense, it is still possible to find resins which are scarcely soluble in acetone and are utilizable in liquid developer, such as certain species of resin-modified phenol formaldehyde resins, linear oil-modified resin-modified phenol formaldehyde resin, styrene-butenediene copolymer, other styrene co-polymer, polyisobutylene, polybutene. When the bleaching bath is chiefly composed of alcohols, the range of selection of resin component in toner can be widened, leaving practically no problem.

The component (II) in the bleaching bath of this invention is thus selected according to the preceding discussion. In the practice potassium hydroxide and then sodium hydroxide are most desirable because of the solubility in said organic solvents.

The concentration of alkali hydroxide in the bleaching bath is generally between 0.01 and 20 wt.%, preferably between 0.1 and 2 wt.%. The bleaching bath with elevated concentration of alkali hydroxide is employed for realizing accelerated treatment.

The addition of (IV) cationic surface active agent is also suitable for treating electrophotographic photosensitive layer containing certain species of dyes.

It is desirable that the bleaching operation can be carried out at a temperature as low as possible since the majority of the solvents belonging to the categories (I) and (III) in the bleaching bath has elevated volatility and may be hazardous to human body when inhaled in a large amount. The bleaching bath according to this invention is particularly effective for the use at the room temperature or therearound, and proves to be far stronger than bleaching solutions using organic acids. Naturally the activity of the bath is increased when higher temperature is employed, but suitable measure against danger should be taken in this case.

Actual procedure of bleaching can be simply carried out by dipping colored electrophotographic photosensitive layer having formed image thereon into the bleaching bath. Stirring of the bath is preferable for realizing effective bleaching. Instead of employing bleaching bath, similar result can be obtained by showing the bleaching solution onto said layer. In some cases, the application of ultrasonic wave is effective for shortening the processing time. The required processing time depends chiefly upon the concentration of alkali hydroxide (II), but it is also dependent on the ratio of the solvents (I) and (III). Besides the amount of cationic surface active agent (IV) is related to the bleaching speed, and thus the addition thereof to the bleaching bath containing the components (I), (II) and eventually (III) enables to obtain the bath of modified bleaching speed. Furthermore the bleaching speed is naturally governed by the temperature.

Succeeding to the bleaching treatment with the bleaching bath of the present invention, it is desirable...
to rinse the treated layer with either one of the solvents (1) and (III) or at least one of said solvents added with acid. This operation assures prolonged storage of the sensitive layer as well as the image thereon without any deterioration afterwards, but further preferable step is to rinse the layer with dilute acid solution. Naturally the use of acid is undesirable for certain dyes, but this operation which intends to neutralize eventually remaining slight amount of alkali, can be satisfactorily realized with acid of very low concentration.

This invention will be further clarified by the following examples.

**EXAMPLE 1**

100 g of zinc oxide, 20 g of vinyl chloride-vinylacetate copolymer and 60 g n-butyl acetate are blended for 10 hours in a porcelain ball mill to obtain white dispersion, which is successively added with 3 mg of fluorescein, 3 mg of rose bengale and 3 mg of brilliant blue FCF dissolved in 10 ml of methyl alcohol. After sufficient agitation, the obtained colored dispersion is appropriately diluted with n-butyl acetate and applied onto aluminum foil to obtain a layer of 10 microns thick after drying. Thus obtained electrophotographic photosensitive layer is colored in pale purple. This layer is subjected to electrostatic charging, image-wise exposure and cascade development with toner containing carbon black followed by heat fixing.

A solution of the following composition:

- Methyl alcohol: 50 ml
- Acetone: 50 ml
- Potassium hydroxide: 0.5 g

is placed in a shallow container, and the photosensitive layer having formed image thereon is dipped in said solution for 30 seconds. After this period, the layer showed black clear image on white background. The layer is successively washed with methyl alcohol-acetone (1:1) mixture and dried.

**EXAMPLE 2**

The white dispersion is prepared in a same manner as in Example 1, which is then added with 3 mg of p-dimethylaminoethylbenzylidene rhodanine, 3 mg of erythrosin and 3 mg of patent blue dissolved in 10 ml of ethyleneglycol monomethyl ether. After sufficient agitation, the prepared colored dispersion is appropriately diluted with n-butyl acetate and applied onto an aluminum foil to obtain a coating of 10 microns thick after drying.

Thus prepared electrophotographic photosensitive layer is electrophotographically processed with a liquid developer respectively containing benzidine yellow GR, brilliant carmine 6B and phthalocyanine blue as toner. The obtained multi-color image lacked whiteness in highlights and suffered from low saturation in other parts.

A solution of the following composition:

- Methyl alcohol: 40 ml
- Ethyl alcohol: 40 ml
- Acetone: 15 ml
- n-butyl acetate: 5 ml
- Potassium hydroxide: 0.5 g

is prepared and used for bleaching of said layer. A bleaching operation of 30 seconds at room temperature results in remarkable bleaching effect, giving improved highlight part and higher saturation. Succeeding washing is carried out using 0.05% solution of succinic acid in ethyl alcohol.

**EXAMPLE 3**

100 g of zinc oxide, 12 g of styrenized alkyd resin (Japan Reichhold, Styresol No. 4400), 8 g of polysiocyanate compound as hardener (Bayer; Desmodule L) and 80 g of n-butyl acetate are blended to obtain white dispersion, which is added then with each 10 mg of fluorescein, rose bengale and brilliant blue FCF dissolved in 5 ml of methanol. After sufficient agitation, the obtained dispersion is applied onto a paper sheet provided previously with subcoating so as to obtain a coating of 10 microns thick after drying. After drying, the binder is hardened by keeping the sheet in a thermostat box of 50°C for 12 hours.

The bleaching effect of a solution of the following composition:

- Methyl alcohol: 30 ml
- Ethyl alcohol: 30 ml
- Acetone: 30 ml
- n-butyl acetate: 10 ml
- Potassium hydroxide: 6.5 g

is measured by applying the same on the photosensitive layer having no image thereon. The said layer prior to bleaching has C.I.E. index of x=0.301, y=0.311 and Y=0.718. The sample treated for 30 seconds at 25°C and then washed with methyl alcohol changed to the values of x=0.304, y=0.315 and Y=0.839, showing improvement both in hue and brightness. Similar measurement using oxalic acid instead of potassium hydroxide shows the results of x=0.295, y=0.314 and Y=0.808, clearly showing the advantages of potassium hydroxide compared with oxalic acid. The same photosensitive layer having multicolor image thereon composed of three toners respectively of benzidine yellow GR, brilliant carmine 6B and phthalocyanine blue shows greater whiteness without deterioration of image itself by the treatment with the bleaching bath containing potassium hydroxide for 30 seconds at 25°C.

**EXAMPLE 4**

The bleaching bath of following composition is prepared:

- Ethyl alcohol: 20 ml
- Methyl alcohol: 20 ml
- Water: 5 ml
- n-butyl acetate: 5 ml
- Sodium hydroxide: 0.5 g

The photosensitive layer of Example 3 is treated with the above-mentioned bleaching bath for 60 seconds at 25°C and then washed with methyl alcohol. The C.I.E. index after processing is X=0.302, Y=0.314 and Y=0.798.

Similar processing with the same bleaching bath added with 0.1 g of cationic surface active agent (Nissun Cution M2-100; Nippon Oil and Fats Company, Ltd., the surface active agent comprising alkyl dimethylbenzyl ammonium chloride) provides the index of x=0.301, y=0.311 and Y=0.777.
What is claimed is:

1. A process for bleaching an electrophotographic photosensitive layer having an image thereon, said image containing a lake pigment soluble in an acid to obtain an improved color print which comprises treating at room temperature the colored electrophotographic photosensitive layer composed of a dispersion comprising zinc oxide, resinous binder and a dye selected from the group consisting of triphenylmethane and xanthenes dyes and p-dimethylaminobenzylidene rhodanine with a bleaching solution containing (I) 30 to 80% by weight of a solvent for said dye and (II) 0.01 to 20% by weight of an alkali hydroxide thereby changing said photosensitive layer substantially white, and then washing the thus treated layer with a washing liquid comprising at least one of said component (I) and (II) an organic solvent capable of dissolving or slightly swelling said resinous binder or with said washing liquid added with acid.

2. A process for bleaching an electrophotographic photosensitive layer having an image thereon, said image containing a lake pigment soluble in an acid to obtain an improved color print which comprises treating at room temperature the colored electrophotographic photosensitive layer composed of a dispersion comprising zinc oxide, resinous binder and a dye selected from the group consisting of triphenylmethane and xanthenes dyes and p-dimethylaminobenzylidene rhodanine with a bleaching solution containing (I) 30 to 80% by weight of a solvent for said dye, (II) 0.01 to 20% by weight of an alkali hydroxide and (III) less than 10% by weight of an organic solvent capable of dissolving or slightly swelling said resinous binder or with said washing liquid comprising at least one of said components (I) and (II) or with said washing liquid added with acid.

3. A process for bleaching an electrophotographic photosensitive layer having an image thereon, said image containing a lake pigment soluble in an acid to obtain an improved color print which comprises treating at room temperature the colored electrophotographic photosensitive layer composed of a dispersion comprising zinc oxide, resinous binder and a dye selected from the group consisting of triphenylmethane and xanthenes dyes and p-dimethylaminobenzylidene rhodanine with a bleaching solution containing (I) 30 to 80% by weight of a solvent for said dye, (II) 0.01 to 20% by weight of an alkali hydroxide and (IV) a cationic surface active agent thereby changing said photosensitive layer substantially white, and then washing the thus treated layer with a washing liquid comprising at least one of said component (I) and (III) an organic solvent capable of dissolving or slightly swelling said resinous binder or with said washing liquid added with acid.

4. A process for bleaching an electrophotographic photosensitive layer having an image thereon, said image containing a lake pigment soluble in an acid to obtain an improved color print which comprises treating at room temperature the colored electrophotographic photosensitive layer composed of a dispersion comprising zinc oxide, resinous binder and a dye selected from the group consisting of triphenylmethane and xanthenes dyes and p-dimethylaminobenzylidene rhodanine with a bleaching solution containing (I) 30 to 80% by weight of a solvent for said dye, (II) 0.01 to 20% by weight of an alkali hydroxide and at least one of (III) less than 10% by weight of an organic solvent capable of dissolving or slightly swelling said resinous binder and (IV) a cationic active agent thereby changing said photosensitive layer substantially white, and then washing the thus treated layer with a washing liquid comprising at least one of said components (I) and (III) or with said washing liquid added with acid.

5. The process as claimed in claim 1 wherein said solvent for said dye is water.

6. The process as claimed in claim 1 wherein said solvent for said dye is methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, ethylenglycol or monomethyl ether.

7. The process as claimed in claim 1 wherein said alkali hydroxide is potassium hydroxide, sodium hydroxide, lithium hydroxide.

8. The process as claimed in claim 1 wherein said organic solvent is aromatic solvent.

9. The process as claimed in claim 1 wherein said organic solvent is ester.

10. The process as claimed in claim 1 wherein said organic solvent is ketone.

11. The process as claimed in claim 8 wherein said aromatic solvent is toluene or xylene.

12. The process as claimed in claim 9 wherein said ester is butyl acetate or ethyl acetate.

13. The process as claimed in claim 10 wherein said ketone is methylethylketone or methylisobutyl ketone.

14. The process as claimed in claim 1 where the concentration of said alkali hydroxide is approximately between 0.01 and 2% by weight.

15. The process as claimed in claim 5 where the concentration of said water in said bleaching solution is less than 10% by weight.