

[54] **DEVELOPING PROCESS USING TONERS AT A REACTOR PRODUCT BETWEEN A DYE HAVING AN AMINO GROUP AND ORGANIC HALIDE**

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Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 63,229, Aug. 12, 1970, abandoned, which is a division of Ser. No. 722,274, April 18, 1968, abandoned.

[52] **U.S. Cl.**..... **117/17.5**, 96/1 SD, 96/1 LY, 117/37 LE, 252/67.1

[51] **Int. Cl.**..... **G03g 9/02**, G03b 9/04

[58] **Field of Search**..... 96/150, 164; 117/17.5, 117/37 LE; 252/62.1

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[57]

ABSTRACT

Toners for developing electrostatic charge images and processes for using said toners to develop electrostatic charge images. The toners comprise compounds produced by the reaction of a dye having an amino group with a halide having more than five carbons, said halide being selected from the group consisting of aliphatic halides, aromatic halides, heterocyclic halides, aliphatic acid halides, aromatic acid halides, and heterocyclic acid halides. Such toners are useful in both wet and dry electrostatic developing processes.

2 Claims, 4 Drawing Figures

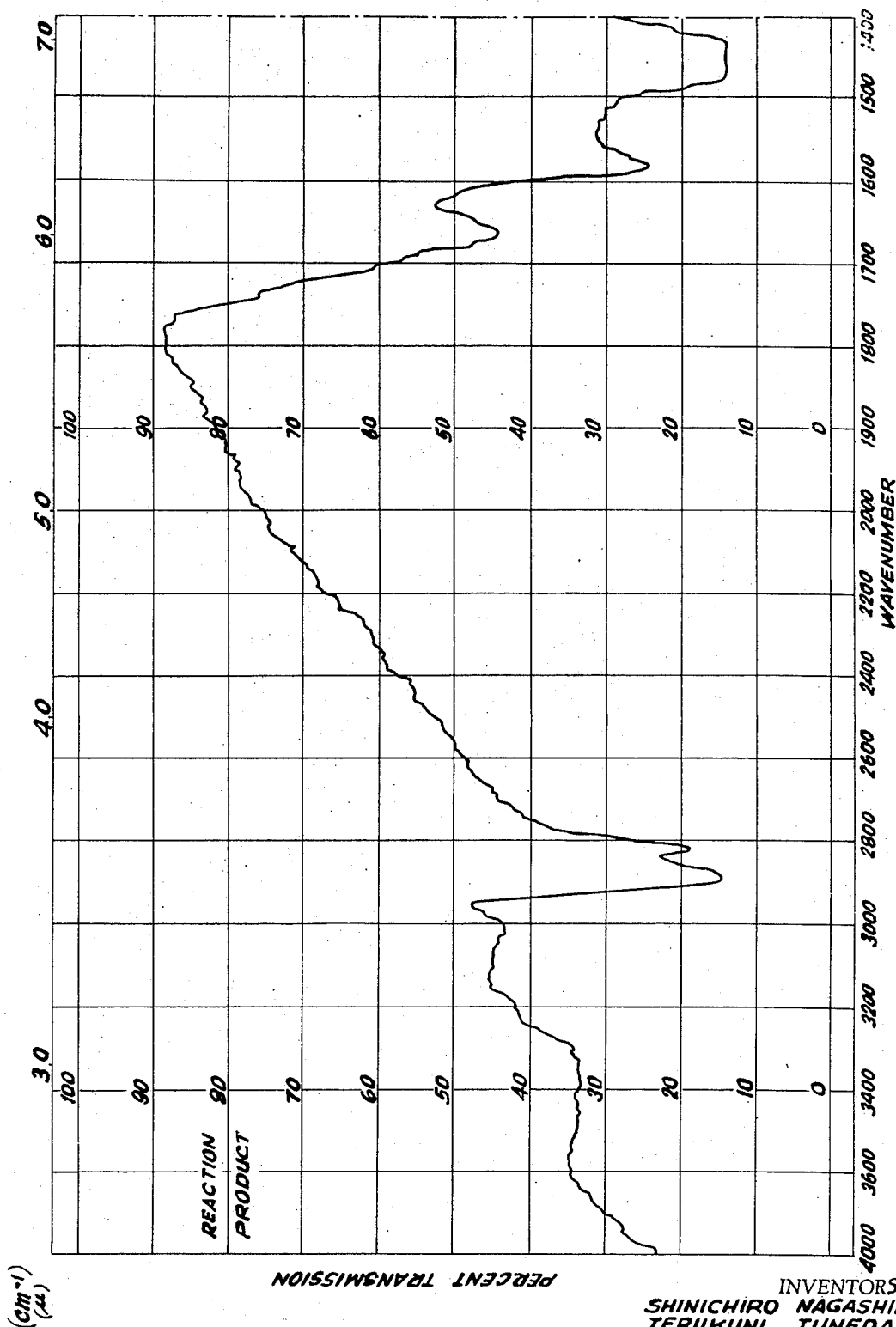


FIG. 1a

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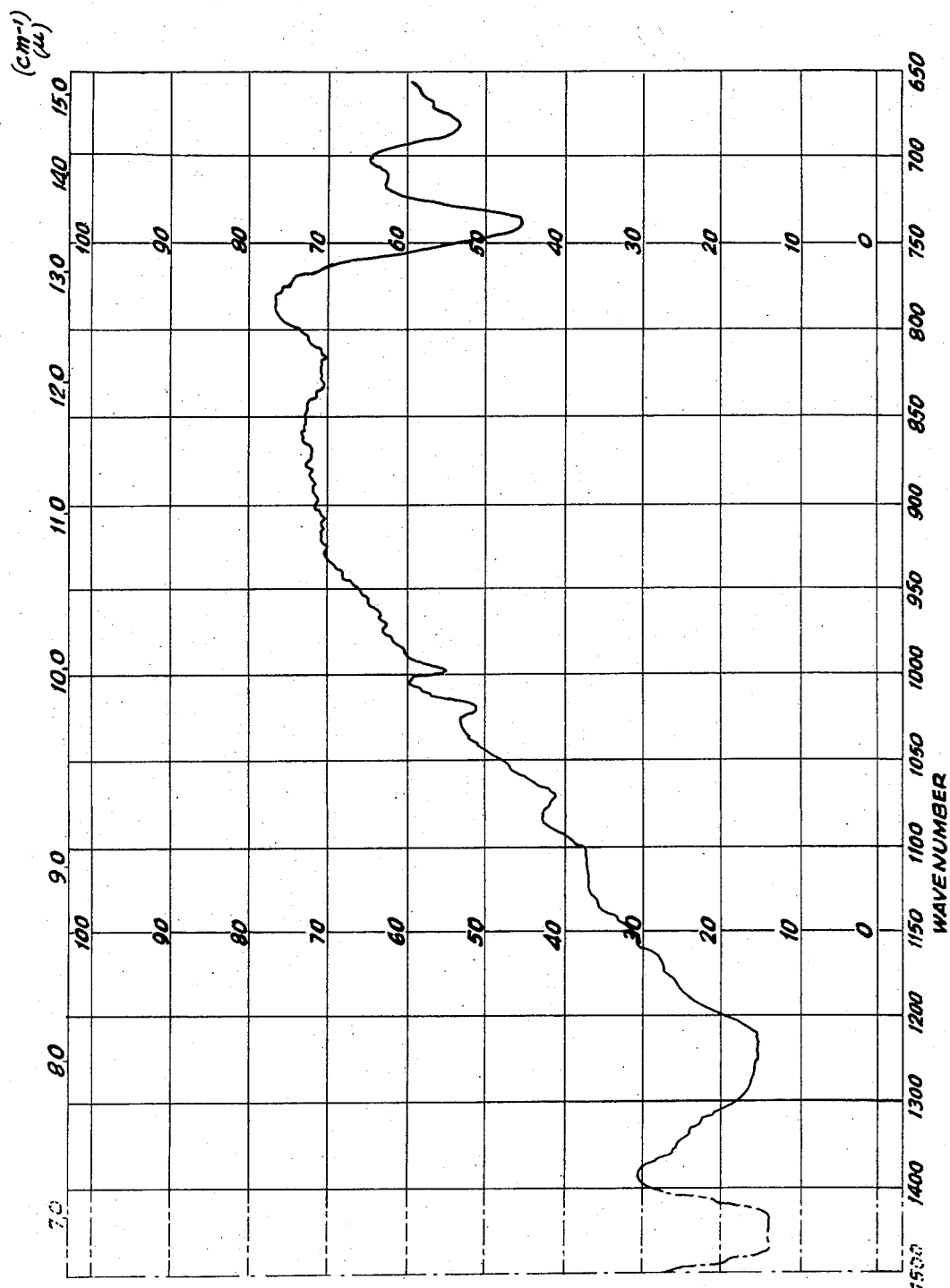


FIG. 1b

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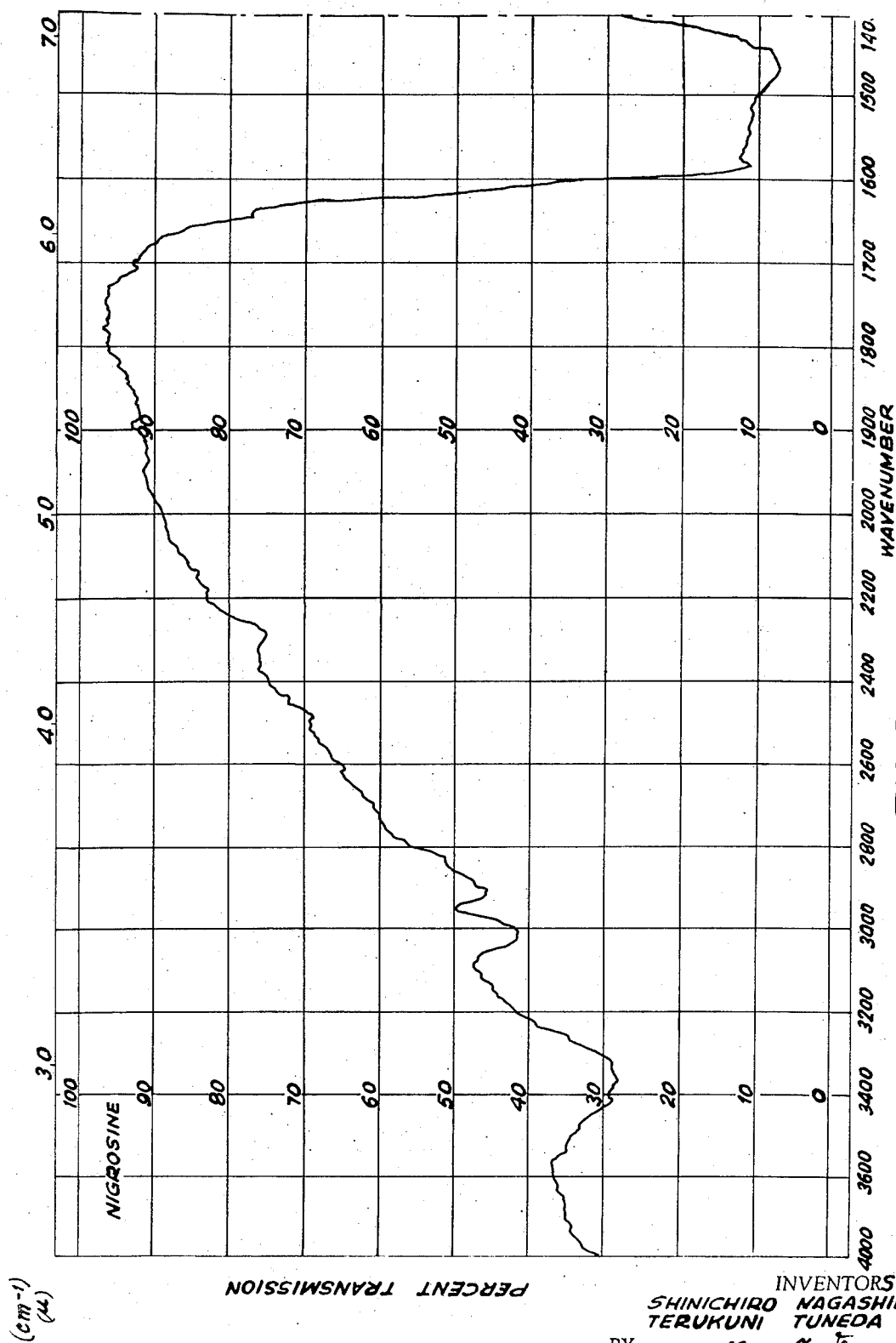


FIG. 2a

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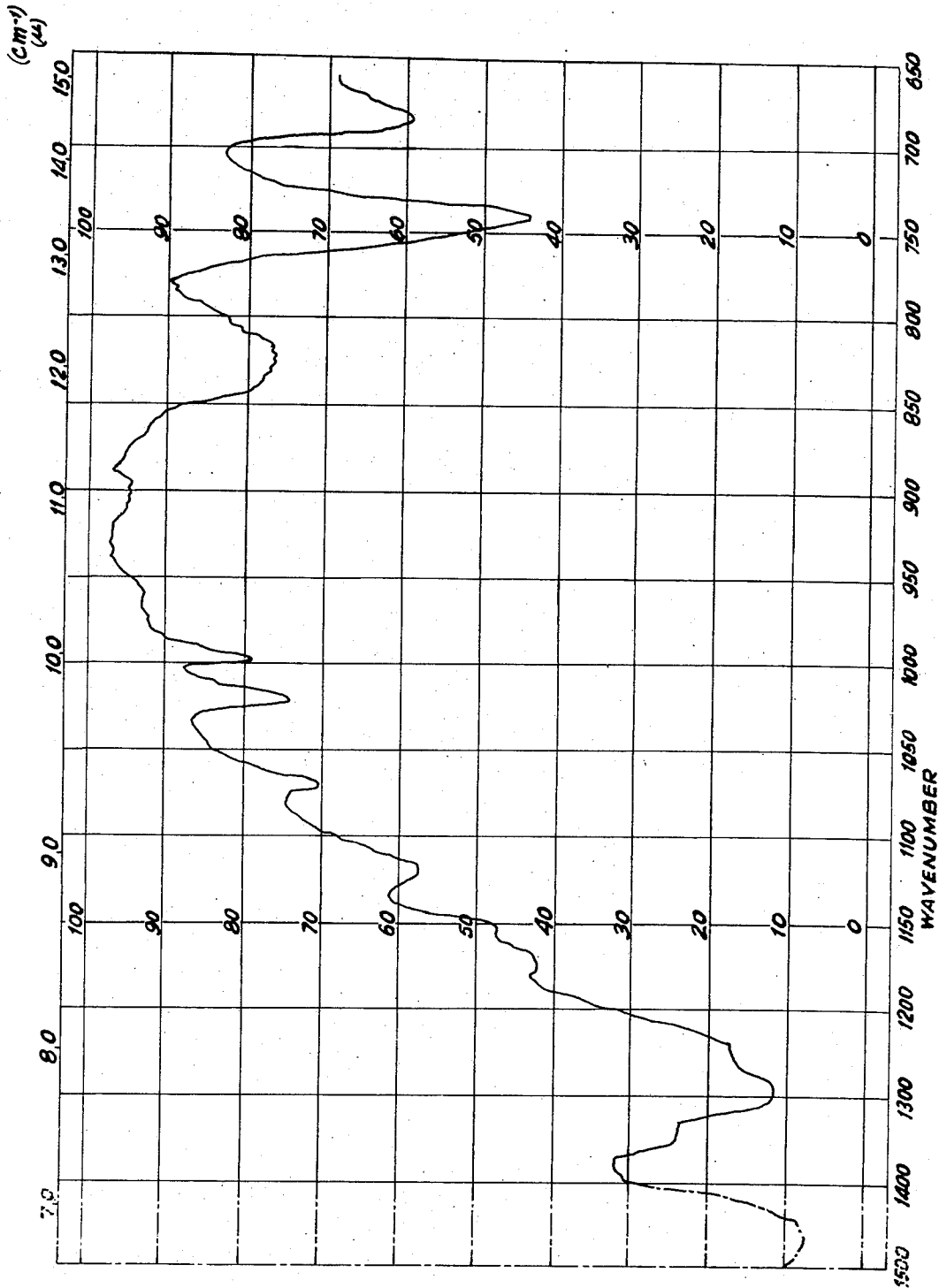


FIG. 2b

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DEVELOPING PROCESS USING TONERS AT A REACTOR PRODUCT BETWEEN A DYE HAVING AN AMINO GROUP AND ORGANIC HALIDE

CROSS-REFERENCE TO PRIOR APPLICATIONS

This is a continuation-in-part of our copending application, Ser. No. 63,229, filed Aug. 12, 1970 now abandoned, which, in turn, was a division of our copending application, Ser. No. 722,274, filed Apr. 18, 1968, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a toner for developing electrostatic charge images obtained in, for example, electrostatic photography, electrostatic recording, electrostatic printing and the like.

As to toners for developing electrostatic charge images, there have hitherto been employed in dry processes, such as magnetic brush processes, cascade processes or powder cloud processes, fine powders of natural or synthetic resins incorporated with coloring matters such as carbon black, while in wet processes fine powders consisting of pigment particles coated with a so-called controller or stabilizer, such as alkyd resin or linseed oil, are used.

As a modern improved type of developer, the so-called liquid-liquid system is the object of attention wherein a liquid colored with dyestuffs or pigments is used as the toner. The toner employed in said liquid-liquid system consists of a solvent, an oil, a fatty acid or a resin containing a coloring material dissolved therein.

As mentioned above, the well-known types of toners are mostly in the form of a suspension or solution consisting generally of a natural or synthetic resin, one of the aforesaid liquid materials and a coloring material suspended or dissolved therein, these toners thus being two-component systems consisting of a medium having fixing ability and a coloring material.

The toners made up of two-component systems are, however, defective in that (1) realization of thoroughly homogeneous dispersion of coloring material in the medium is a matter of great technical difficulty and also in that (2) the developed images are liable to be obliterated, for example, through rubbing. Thus, speaking for example of a dry type of toner composed of polystyrene resin and carbon black, a solid polystyrene resin is first melted by heating and mixed with carbon black which is dispersed by thoroughly kneading the mixture. The dispersion thus obtained as black lumps is treated with a crusher to yield a finely divided product which is employed as the toner. However, despite the fact that the hot melt of the resin is kneaded together with carbon black with the help of a high efficiency dispersing machine like a roll mill, even when the kneading operation is carried out by highly skilled workers for a long time, numerous grains of a secondary aggregate of carbon black particles remain persistently in the dispersion product and make it technically impossible to produce a perfectly homogeneous dispersion. Moreover, as the carbon black particles agglomerated into a secondary aggregate are also liable in the process of crushing to become separated from the binding medium, there are present in the toner product foreign particles of carbon black which behave to obstruct toner fixing. In the case of liquid developers, on the other hand, carbon black is kneaded in a wet system together with an alkyd

resin by means of a high efficiency dispersing machine such as a roll mill or colloid mill and the pasty mixture obtained is dispersed in a carrier liquid, such as a petroleum hydrocarbon, to yield a suspension. Also in this case, however, it is almost impossible for the carbon black to be homogeneously dispersed in the alkyd resin, and the toner inevitably contains secondary aggregates of carbon black and therefore is in a state of imperfect dispersion.

As the images developed by means of the conventional, imperfectly dispersed toner are liable, when strongly rubbed or scratched on the surface, to release carbon black from the fixing medium, they become filled with many lines and are thus disagreeable in appearance.

Although liquid developers of liquid-liquid systems wherein, in most cases, the coloring material is dissolved in a liquid phase scarcely have such weaknesses to rubbing as mentioned above, they are also defective in that when a solvent like alcohol which dissolves the coloring material is dropped onto the developed image, the coloring material becomes partly dissolved to cause the image to be blurred and smudged.

Recently, in an effort to resolve these defects, a method described in the specification of British Patent 1196749 was proposed, wherein a substance prepared by making a reactive binding medium and a reactive coloring material chemically combine with each other is put to use as toner. As these toners of chemical combination systems are prepared by means of various syntheses and are in general simple substances produced by chemical combination between a binding medium and coloring material both being in the molecular state, they are in a perfect state of dispersion, assuring that even in the process of grinding to a fine powder the coloring material does not separate from the binding medium, and therefore exhibit excellent stability, reproducibility and developing power. However, in this chemical combination system it cannot be said that any binding medium and any reactive coloring material may be used, as the reaction between them to provide a toner suitable for practical use may be difficult. Thus, depending on the choice of binding medium and reactive coloring material, the performance of the toner obtained may have various deficiencies such as the following: The reaction for chemical preparation of the toner proceeds at an extremely slow rate; the reaction product is apt to decompose, discolor or is unable to produce the desired tone of color; electric charges of the same polarity as the electrostatic charge image to be developed are produced to prevent the obtaining of a positive image by providing an undesired negative image; chance dissipation of the electric charge leads to a bare appearance or a light image; however good the developed image may be, the toner is too expensive to be used commercially.

SUMMARY OF THE INVENTION

The present inventors have synthesized various kinds of toners of the chemical combination type system and through inspection of the developing power and the practicality of the toner products have arrived at the discovery that a series of synthetic substances prepared according to the present invention are suitable for use as toners in the development of electrostatic charge images.

Accordingly, the main object of the present invention is to provide toners of the chemical combination type system that are highly suitable for performing dry or wet development of electrostatic charge images.

Another object of the invention is to provide chemical combination type toners which are prepared from mutually reactive ingredients without requiring any costly dispersing machine and highly skilled operation and which are excellent in producibility as well as practical.

A further object of the present invention is to provide chemical combination system toners which are substantially free from danger of decomposition, discoloration, decoloration and blurring and which are stable and excellent in reproducibility.

Another object of the invention is to provide chemical combination system toners which are charged with electricity in an extremely stable state and which are comparatively low in price.

Another object of the invention is to provide homogeneous black toners and a further object is to provide homogeneous toners colored other than black.

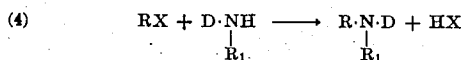
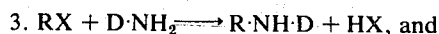
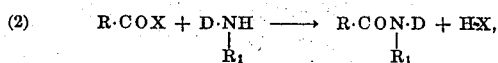
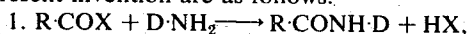
Another object of the invention is to provide chemical combination system toners which are possessed of excellent fixing ability.

Objects and features of the present invention will be more fully understood from the following detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides novel toners which not only overcome any defects hitherto inevitably met with but also prove to be highly practical. A mode of embodying the invention comprises the preparation of a toner for developing electrostatic charge images, said toner containing the product obtained by chemically combining a saturated or unsaturated, substituted or unsubstituted aliphatic, aromatic or heterocyclic halide or acid halide having more than 5 carbon atoms and a dyestuff containing a primary or secondary amino group.

Typical examples of the reaction according to the present invention are as follows:



wherein R and R₁ represent an aliphatic, aromatic or heterocyclic group, D represents the non-amino portion of a dye molecule and X stands for a halogen atom.

As will be perceived from the above equations, reaction products according to the present invention are formed by the chemical combination of an aliphatic, aromatic or heterocyclic molecule with a dyestuff wherein the aliphatic, aromatic or heterocyclic moiety confers a fixing ability to the toner. Typically, the reaction may be carried out by first mixing the acid halide and the dye at relatively low temperatures, e.g., from

about 0°–10°C, and thereafter completing the reaction at a temperature from about 90°–150°C.

As typical examples of the halide or acid halide type of aliphatic, aromatic or heterocyclic compound, there may be mentioned propionyl chloride, butyryl chloride, valeryl chloride, capronyl chloride, capryl chloride, succinyl chloride, adipoyl chloride, cinnamoyl chloride, phthaloyl chloride, propyl chloride, propyl bromide, butyl chloride, isobutyl bromide, t-amyl chloride, hexyl bromide, octyl chloride, lauryl chloride, stearyl chloride, stearyl bromide, oleyl chloride, adipyl chloride, bromoanisole, bromodimethylaniline, dichlorobenzene, trichlorobenzene, phthalyl chloride, 2-methyl quinoline-4-carboxylic acid chloride, antipyrinic chloride, di-pyrrolic chloride, furancarboxylic acid chloride, etc. Any one or more members of these substances may enter the chemical combination.

As mentioned above, the dyestuffs employed according to the present invention are those which have a primary or secondary amino group and are represented by such dyes as the following: Acidic azo-dyes such as Anthracene Red. G.G., Quinon Fast Red 4 BL and Supramine Red BBL, direct azo-dyes such as Direct Violet O, Benzopurprin 8B and Diamine Black RO, basic azo-dyes such as Chrysoidine, Bismarck Brown G and Bismarck Brown R, dyes of the anthraquinone series such as Alizarin Fast Blue R, Antraquinone Blue SRX, Alizarin Sky-blue B and Alizarin Direct Blue, indigoid-dyes such as Indenthrene Grey 6B, sulphide-dyes such as Sulfur Black T, dyes of the triphenylmethane series such as aniline blue and parafuchsin, quinoneimine-dyes such as Safranin T, aniline black, Indulin 5 and nigrosines, dyes of the phthalocyanin series such as tetra (4) amino copper phthalocyanin blue, etc.

Further, the toners of the present invention can be obtained in a solid, semi-solid or in a liquid state depending, for example, on the number of carbom atoms in the alkyl group and the molecular structure of the dye moiety and also depending on other factors such as reaction conditions. The toners of the invention can thus be applied to various types of processes such as dry processes with a solid-solid system, cloud processes with a solid-gas system, liquid processes with a solid-liquid system, emulsion processes with a liquid-liquid system and fog processes with a gas-liquid system.

The present inventors found, moreover, that in obtaining black toners which are most widely used in practice, it is advantageous to react halides of fatty acids, chlorides of fatty acids in particular, and nigrosine base which turns black as the reaction with the chloride of fatty acid proceeds. A satisfactory tone and deepness of color can be obtained even without resort to the carbon black heretofore in use.

It is also possible by changing the relative amount of the chloride of fatty acid to the nigrosine to obtain the product in any state extending from solid to liquid. Generally, with an acid halide to dye ratio in the range from about 1:1 to 4:1, a solid toner is obtained, whereas when the ratio ranges from about 4:1 to 8:1, a product varying from a semi-solid or paste to a liquid can be obtained. Understandably, these ratios can vary slightly depending on the specific compounds being used. Thus, for example, the combination of oleyl chloride and nigrosine in the ratio 2:1 by weight leads to a solid product; in the ratio 4:1 leads to a semi-solid product; in the ratio 6:1 leads to a paste and the combination in the ratio 8:1 leads to a liquid toner product. The solu-

bility in solvent of the toner product varies according to the ratio by weight in which the two ingredients are combined with each other. The just mentioned delicate variation of solubility is of great significance especially in the preparation of liquid developers of the emulsion type.

Thus, when the solvent is a petroleum consisting mainly of isoparaffins having a carbon number of about 12, the optimum effect is achieved by the reaction products obtained by using oleyl chloride and nigrosine in the ratio 6:1 or so. All of these reaction products have a good black appearance and no trace of the violet peculiar to the unreacted nigrosine.

As to the method of applying the toners of the present invention onto electrostatic charge images, there may be mentioned as well-known both dry methods and wet methods. In carrying out the dry methods, a composition prepared by mixing iron fillings or glass beads with the toner so that a toner content of 1-10% by weight is obtained is contacted according to the magnetic brush process or according to the method of cascade development with the surface carrying the electrostatic charge image, or alternatively, the toner, finely dispersed in air, is applied by the method of powder cloud development.

After the application, the surface carrying the thus applied toner is heated so as to melt and thus fix the toner. It should be noted at this point that no separate fixative agent is required in the dry developer of the present invention. Thus, the toner of the present composition is formed from a single component which is melted by heat during the fixation step.

In carrying out the wet methods, on the other hand, the toner which may be a solid, semi-solid, or liquid is dispersed in a carrier liquid like petroleum, for example, which has a high electrical resistance and is not destructive to electrostatic charges so as to provide a solid or liquid dispersion. The dispersion thus prepared is applied onto the surface carrying the electrostatic charge image by following the imbibition method, roller method, spray method and the like.

The carrier liquid is not a solvent for the developer. Rather, in the case of a liquid toner, it is only necessary that the toner be dispersed in the carrier liquid, but not dissolved by it. In the case of a solid toner being used with a liquid carrier, it is sufficient that the carrier liquid merely disperse and swell the solid toner.

After application of the dispersed toner, complete fixation is accomplished by rapid vaporization of the carrier liquid by warm air. This is, of course, the conventionally used method. Typically, most of the carrier liquid is removed by use of a squeeze roller after development in the development liquid. The paper with the toner thereon is then heated with warm air to evaporate the carrier liquid.

In these cases, the chemical combination system toner of the present invention acquires positive or negative charges originating in frictional electricity or in boundary surface electric potential arising from the contact of the toner with the carrier substance, e.g. iron powder, glass beads, air or petroleum, and is selectively attracted or repelled according to whether the electrostatic image is charged oppositely or similarly in sign to the toner, resulting thereby in the visualization of the image. In principle, an apparent positive image is obtained in the former case and an apparent negative image in the latter.

In a specific example of wet development, it is possible to use as the carrier a conductive liquid like water.

The chemically reacted toner of this invention can be further chemically treated for the purpose of selecting an electrostatic charge so as to control the electrostatic charge relative to the electrostatic image.

The chemical treatment for selecting an electrostatic charge is to introduce electron attracting groups or electron donating groups in the chemical structure, and it is carried out on either the fixing medium material or the coloring material before the reaction of the two, during the reaction or to the reaction product after the reaction.

There are chemical treatments such as the above for removing a part or the whole of electron attracting groups or electron donating groups already existing in the fixing medium material or coloring material or for adding the same, or for partially or wholly changing the same.

A number of publications in the field of organic chemistry disclose electron attracting groups and electron donating groups, and the following are typical examples thereof;

Electron attracting groups: Nitro group, carboxyl group, cyano group, hydroxyl group, halogen atom.

Electron donating groups: Amino group, ammonium group, sulfonium group, oxonium group, phosphonium group, pyridinium group.

The present invention will be explained in more detail by the following examples. It is not intended, however, to limit the scope of the invention thereto.

EXAMPLE 1

Reaction of oleyl chloride with nigrosine

Five parts of sufficiently dried nigrosine were dissolved in 150 ml of dioxane. Then 5 parts of triethylamine were added with stirring to this solution which was cooled to 0°-10°C. To the mixture were added 5 parts of oleyl chloride dropwise and at a slow rate. After letting the reaction mixture stand for 30 minutes, it was brought to a temperature of 90°-100°C, stirred at this temperature for 4 hours and thereafter allowed to cool.

The liquid was filtered and trimethylamine hydrochloride and dioxane were removed from the filtrate under reduced pressure to leave a black sticky residue. By recrystallizing the black material from a hot mixture of benzene and methanol, a black pasty product was obtained. IR spectrum of this product showed an absorption at 1,670 cm^{-1} indicative of the presence of an amide group, the product being thus corroborated as a chemically combined substance.

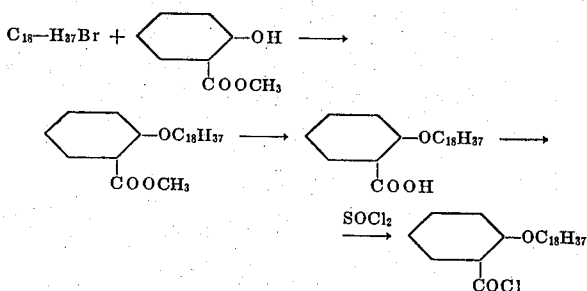
0.5 part of the pasty product thus obtained was dispersed in 100 parts of isoparaffin solvent, a developing toner liquor being obtained. When an electron photo paper carrying a negatively charged electrostatic latent image was treated with this liquid toner, a black positive image was developed which was very sharp and distinct, particularly excellent in the reproducibility of half tone and found to be perfectly fixed on the photo paper.

The infrared spectrograph of the product (C 78.5%, H 7.9% N 7.8% Ash 0) produced by the reaction of myristyl chloride with nigrosine in a similar way to the above is shown in FIGS. 1a and 1b, and a similar spec-

trograph of nigrosine (C 77.8% H 4.2% N 11.4% Ash 21 μ g) is shown in FIGS. 2a and 2b.

EXAMPLE 2

Reaction of a stearyl bromide modified acid halide and nigrosine.



In a four-mouthed 500 ml flask equipped with a stirrer and reflux condenser, sodium alcoholate is prepared from 200 parts of absolute alcohol and 8g of metallic sodium. After the addition of 53 parts of methyl salicylate and 117 parts of stearyl bromide, the reaction mixture is heated for 24 hours under reflux. After the mixture is allowed to cool, it is poured into a solution composed of 600 ml of water and 12 ml of concentrated hydrochloric acid. By extracting with ether, 140 parts of yellow oil were obtained. This oil was added to 30 parts of potassium hydroxide, 70 parts of water and 70 parts of alcohol and hydrolyzed by heating for 3 hours under reflux, 152 parts of 2-octadecylic benzoic acid being thereby obtained. To 58 parts of the 2-octadecylic benzoic acid, 119 parts of thionyl chloride were added and the mixture was heated for 3 hours under reflux and then the excess of thionyl chloride was removed. 61 parts of the corresponding acid chloride were thereby obtained.

In a four-mouthed 200 ml flask, 5g of well dried nigrosine were dissolved in 150 ml of dioxane and added to this were 5 parts of triethylamine. After the mixture was cooled to 0° – 10° C, to it were slowly added 6 parts of the above chloride product. The mixture was then heated under reflux at 90° – 100° C for 4 hours and thereafter allowed to cool. The reaction mixture was then filtered and the filtrate was freed from dioxane and triethylamine. A black sticky matter was thereby obtained which yielded a black pasty product after recrystallization from a hot mixture of benzene and methanol. According to the result of chromatographic assay with ethylacetate-cellosolve (1:1) developing liquid, this product gave only a single black spot, while the nigrosine employed as starting material was divided into seven components, yellow, orange, pink, red, violet, blue and black in color, respectively. These data are indicative of the formation of a single black substance through the chemical reaction of the present invention.

A liquid developer was prepared by dispersing 0.5 part of this paste in 100 parts by volume of isoparaffin solvent. With this liquid developer, a sheet of electron photo paper carrying a negatively charged electrostatic latent image was treated, and a positive image with excellent blackness was developed.

EXAMPLE 3

Reaction of oleyl chloride and aniline black

Ten parts of aniline hydrochloride are dissolved in water, 5 parts of concentrated hydrochloric acid are added and the solution is made up to a total volume of 300 ml. To the solution are then added 10 parts of aqueous hydrogen peroxide (30%), the mixture is agitated for one hour, another 10 parts of aqueous hydrogen peroxide are added and the mixture is agitated at 35° C for 4 hours. The mixture turns black owing to the formation of aniline black. The product, aniline black, is removed by filtration, washed with water and dried. 2 parts of the aniline black product are dissolved in 150 parts of dry pyridine. To this solution are slowly added, under cooling at 0° – 10° C, 7 parts of oleyl chloride. After 30 minutes, the mixture is stirred at 140° – 150° C for 4 hours. When the reaction is completed, the mixture is allowed to cool and is acidified by addition of concentrated hydrochloric acid to cause the reaction product to be separated as a precipitate. The precipitate is thoroughly washed with water, dried and washed further with isoparaffin solvent, a dark brown paste being thereby obtained. A liquid developer is prepared by dispersing 0.5 part of the paste thus obtained in 100 parts by volume of isoparaffin solvent. With this liquid developer a sheet of electron photo paper carrying a negatively charged electrostatic latent image is treated, an excellent negative image being thereby developed.

EXAMPLE 4

Reaction of isostearyl chloride and nigrosine

In a four-mouthed 1 liter flask equipped with a reflux condenser, thermometer and stirrer, 30 parts of dry nigrosine dissolved in 800 parts of dry dioxane are added to 30 parts of dry triethylamine. While kept at 0° – 10° C, the mixture has added thereto 60 parts of isostearyl chloride dropwise. The mixture is stirred for 30 minutes, then brought to a temperature of 95° – 100° C, agitated at this temperature for 4 hours and then allowed to cool. When the filtrate obtained by filtering the reaction mixture is concentrated under reduced pressure and has added thereto aqueous methanol with a water content of 20%, a black viscous material is precipitated. The black viscous material is then washed 2–3 times with 95% methanol and dried to produce a black powdery product. 5 parts of this black product are added to 100 parts of cyclohexane and dispersed therein with the help of a ball mill over about a 10-day period. A liquid developer is prepared by dispersing 10 parts of the paste thus obtained in 1,000 parts of cyclohexane. When a sheet of electron photo paper carrying a negatively charged electrostatic latent image is treated with this liquid developer, a positive black image is obtained which is excellent in image securing ability as well as in fixing stability.

EXAMPLE 5

Typical example of a supplementary reaction on the reaction product from nigrosine and a fatty acid halide

In a four-mouthed 1 liter flask furnished with a reflux condenser, thermometer and stirrer, a solution of 41 parts of dry nigrosine in 800 parts of dry dioxane is added with 30 parts of dry triethylamine. After cooling the mixture to a temperature of 0° – 10° C, to it are added, dropwise, 25 parts of acrylyl chloride and the mixture is agitated for 30 hours. The mixture is then stirred at 95° – 100° C for 4 hours and thereafter allowed to cool. The reaction mixture is filtered and water is

added to the filtrate, causing a black precipitate to separate. This precipitate is washed with methanol and dried to yield a black powdery product. 7.8 parts of this powder are dissolved in 200 parts of dimethylformamide and added thereto are 16 parts of lauryl amine. The mixture then has added to it an alcoholate prepared from 0.05 part of metallic sodium and 10 parts of tertiary butanol and the mixture is heated at 120°–130° C for 30 hours with stirring. After cooling, the reaction mixture has water poured into it to cause production of a black precipitate which is then separated by filtration. On thoroughly washing the precipitate with methanol followed by drying, a black powdery product is obtained. 5 parts of this powder are subjected, together with 100 parts of an isoparaffinic solvent, to milling by means, for example, of a ball mill for a period of about 10 days. 10 parts of the pasty product thus obtained are dispersed in 1,000 parts of an isoparaffinic solvent, a liquid developer being thereby prepared. When a sheet of photo paper impressed with a negative charge to form an electrostatic latent image is treated with this liquid developer, a positive black image is developed which is excellent in image securing as well as stability of fixing onto the photo paper.

EXAMPLE 6

Reaction of myristyl chloride and insulin

In a four-mouthed 200 ml flask fitted up with a reflux condenser, thermometer and stirrer, a solution of 7 parts of dry insulin dissolved in 150 parts of dry dioxane is added with 13 parts of dry triethylamine. To the mixture, kept at a temperature of 0°–10°C, are added dropwise 13 parts of myristyl chloride. After stirring the mixture for 30 minutes, it is brought to a temperature of 95°–100°C, at which point it is again stirred for four hours. After cooling, the reaction mixture is filtered. When the filtrate is concentrated under reduced pressure and has added thereto aqueous methanol containing 20% of water, a dark green viscous material precipitates. The precipitate is then washed 2–3 times with hot 95% methanol and then dried to give a powdery product. 5 parts of this powder are subjected, together with 100 parts of an isoparaffinic solvent, to milling by a ball mill for about 10 days to yield a pasty product. A liquid developer was prepared by dispersing 10 parts of the paste in 1,000 parts of an isoparaffinic solvent. When this liquid preparation is applied to a sheet of electron photopaper carrying a negatively charged electrostatic latent image, a positive black image is developed which has excellent image securing ability and stability of fixing onto the photopaper.

EXAMPLE 7

Five parts of well dried nigrosine are dissolved in 150 ml of dioxane and added thereto are 5 parts of triethylamine. The mixture is cooled to 0°–10°C and added dropwise and slowly with stirring are 5 parts of oleyl chloride. After letting the mixture stand for 30 minutes, it is heated to 90°–100°C, stirred at this temperature for 4 hours and then allowed to cool. The liquid is filtered and the filtrate is freed under reduced pressure from triethylamine and dioxane to yield a black viscous material. By recrystallizing this black material from a hot mixture of benzene and methanol, a black pasty product is obtained. 0.5 part of this paste is dispersed together with 0.1 part of hydrogenated resin (commercial name: Staybelite resin) in 100 parts of isoparaffin sol-

vent and milled over a period of 10 days in a ball mill. 20 parts of the dispersion thus prepared are mixed with 1,000 parts of isoparaffin solvent. When the developer liquor thus obtained is used in the same way as in Example 1, a black positive image is obtained which is quite satisfactory due to the controlling effect of the hydrogenated resin upon the charges of the developer particles.

EXAMPLE 8

Synthesis between erucyl chloride and nigrosine

In a four-mouthed 1 liter flask, a solution of 40 parts of dry nigrosine in 800 parts of dry dioxane is added to 24 parts of dry triethylamine. The mixture then has added to it dropwise, while kept at a temperature of 0°–10°C, 45 parts of erucyl chloride. The mixture is then stirred for 30 minutes. After stirring the mixture at 95°–100°C for 4 hours, it is allowed to cool. The filtrate obtained by filtering the reaction mixture is added to aqueous methanol with a water content of 20% and a black viscous material precipitates. On washing this precipitate 2–3 times with 95% methanol followed by drying, a black powdery product is obtained. This black powder is further ground in a ball mill to become of an average particle size of 10 μ , and then mixed with reduced iron powder having an average particle size of 200 μ . When a negatively charged electrostatic latent image on electron photo paper is subjected to development with this powder mixture by the magnet brush technique, a very satisfactory positive black image is obtained. The fixation in this case was effected in the conventional manner by merely heating the paper with the developer thereon so as to melt the toner.

The developing toners of the present invention, being useful not only in electrostatic photography but also for the visualization of various electrostatic charge images such as those which are provided in the so-called chargeless process, pip process, electrostatic printing, electrostatic recording, etc., always exhibit an excellent developing effect. It is beyond question, therefore, that modifications and applications concerning this invention which are easily inferable for those skilled in the art without departing from the spirit of the invention are comprised within the scope of the present invention.

What is claimed is:

1. A process for developing electrostatic latent images by contacting a surface having an electrostatic latent image thereon with a developer prepared by mixing a carrier selected from the group consisting of iron filings and glass beads with about 1 to 10% by weight of a toner for electrophotographic development, said toner being a solid compound produced by the reaction of an acid halide selected from the group consisting of aliphatic acid halides having more than five carbon atoms and aromatic acid halides having more than five carbon atoms, and a dye selected from the group consisting of quinoneimine dyes, the reaction being carried out by first mixing the acid halide and dye at a temperature in the range from about 0° to 10°C, and thereafter, reacting the mixture at a temperature in the range from about 90° to 150°C, the weight ratio of acid halide to dye being from about 1:1 to 4:1, and after said contacting step, heating said surface with the developer thereon so as to melt the toner whereby fixation of the developer to the surface carrying the image is effected.

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2. A process for developing electrostatic latent images by contacting a surface having an electrostatic latent image thereon with a developer prepared by dispersing a toner for electrophotography into a petroleum liquid having an electric resistance large enough so not to destroy the electrostatic latent image, the toner being a solid or liquid compound produced by the reaction of an acid halide selected from the group consisting of aliphatic acid halides having more than five carbon atoms and aromatic acid halides having more

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than five carbon atoms and a dye selected from the group consisting of quinoneimine dyes, the reaction being carried out by first mixing the acid halide and the dye at a temperature in the range from about 0° to 10°C, and thereafter reacting the mixture at a temperature in the range from about 90° to 150°C, the weight ratio of acid halide to dye being in the range from about 1:1 to 8:1, and after said contacting step, removing the petroleum dispersing liquid from the surface.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,793,048 Dated February 19, 1974

Inventor(s) Shinichiro Nagashima et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading of the patent, insert

--[30] Foreign Application Priority Data

April 22, 1967 Japan.....Sho 42-25512--

Signed and sealed this 30th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents