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Hochberg

[11] **3,890,240**

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[54] **TONER COMPOSITIONS AND METHODS FOR THEIR PREPARATION**

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[21] Appl. No.: **38,098**

Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 597,240, Nov. 28, 1966, abandoned, and Ser. No. 597,247, Nov. 28, 1966, abandoned.

[52] **U.S. Cl.** **252/62.1**

[51] **Int. Cl.²** **G03G 9/04**

[58] **Field of Search** ..... 252/62.1; 117/37 LE

[56] **References Cited**

UNITED STATES PATENTS

2,891,911	6/1959	Mayer	252/62.1
3,241,957	3/1966	Fauser et al.	252/62.1
3,244,633	4/1966	Yellin et al.	252/62.1
3,259,531	7/1966	Matkin	252/62.1
3,378,513	4/1968	Witwer	260/33.3

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[57] **ABSTRACT**

A toner composition for use in electrophotography is provided which contains finely divided pigment, which may advantageously be carbon black in the form of agglomerates or flocculates together with a colorant, preferably a basic triarylmethane dye such as Victoria Blue B Base but which may be an alizarin water-soluble dye, suspended in a volatile isoparaffinic hydrocarbon vehicle having both an acrylic terpolymer resin and at least one polyvalent metal soap dissolved therein and having an electrical resistivity between about 1×10^9 and 1×10^{12} ohm-cm., part or all of the agglomerates or flocculates advantageously being of a size that will produce high image density but preferably a part thereof being of a smaller size producing good fill-in.

Blue toners, preferably containing 'Alkali Blue RS pigment, and red toners which contain Cadmium Red pigment are provided. Black toners capable of making intense black prints may be obtained by admixing a minor proportion of the blue toner with a major proportion of the black toner.

The toners are produced by milling the pigment and dye with a concentrated solution of the terpolymer with or without the metal soap in the hydrocarbon solvent, diluting the resulting mill base with sufficient additional metal soap-containing hydrocarbon to form a toner concentrate, subjecting this to high frequency agitation if improved fill-in is desired, and finally diluting it to working strength by admixture with more of the hydrocarbon.

6 Claims, 4 Drawing Figures

Fig. 1.

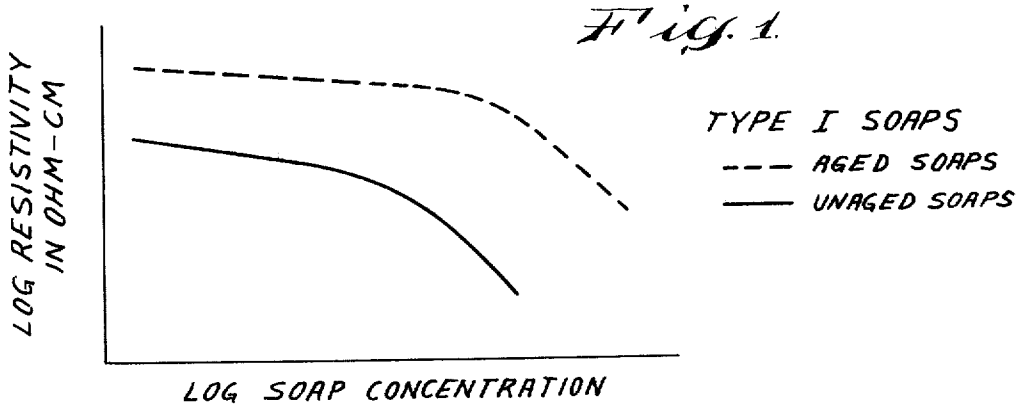


Fig. 2.

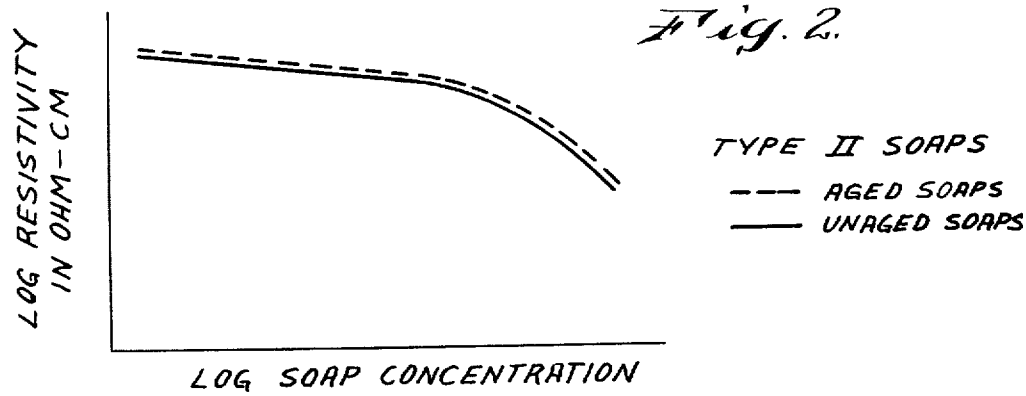
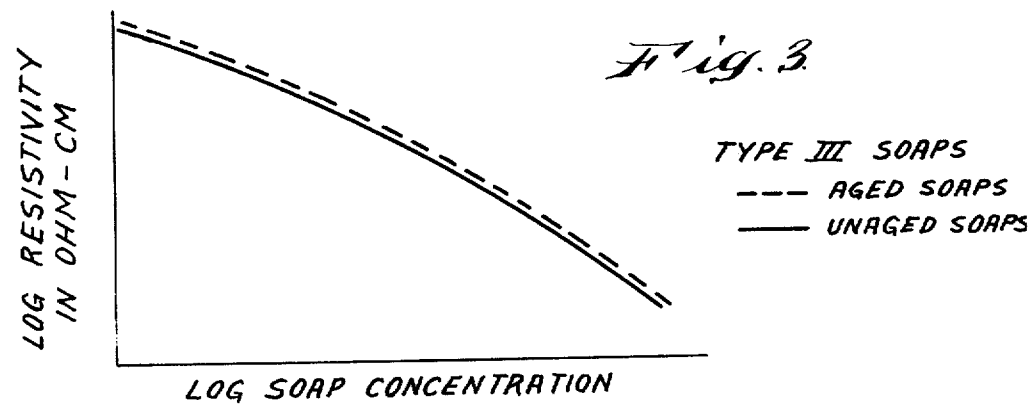
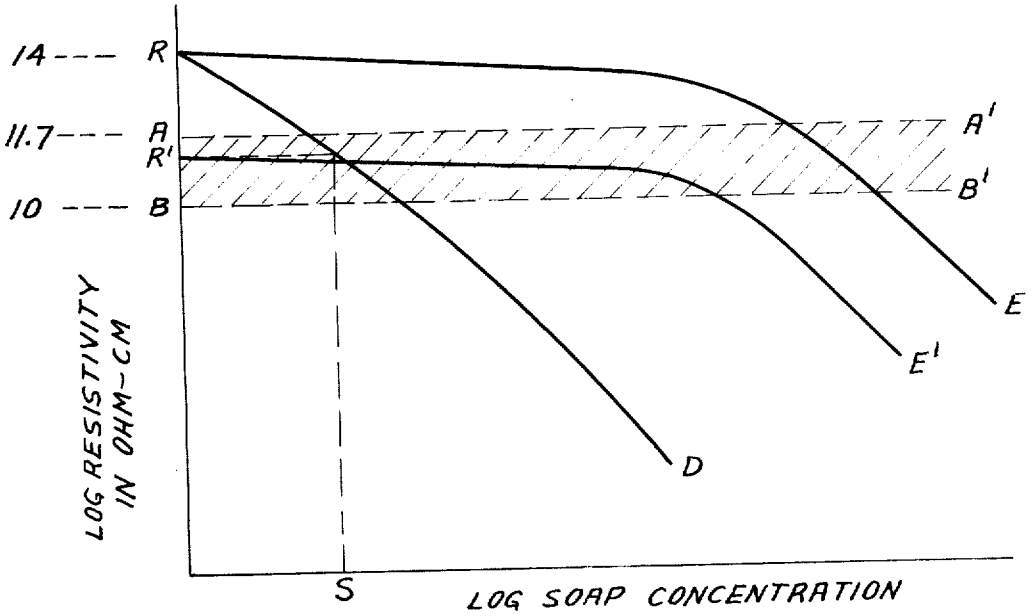


Fig. 3.



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Fig. 4



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TONER COMPOSITIONS AND METHODS FOR THEIR PREPARATION

This is a continuation-in-part of my copending applications Ser. Nos. 597,240 now abandoned and 597,247 now abandoned both filed Nov. 28, 1966.

This invention relates to toners for use in electrophotography, and more particularly to compositions of this type wherein finely divided pigment is suspended in a volatile hydrocarbon liquid having a high electrical resistance. The invention includes the toner compositions themselves, as will hereinafter be more fully described, as well as methods for their preparation and methods for developing latent electrostatic images wherein they are used.

In electrostatic printers a photoconductive layer is given an electrostatic positive or negative charge in the dark, such as by means of a corona-charging device. The charged layer is then exposed to a light image of the original document to cause the charge on the layer to leak off in non-image areas and leave a latent electrostatic charge image on the layer. This image is then developed by applying to the photoconductive layer a toner containing particles which have a charge opposite to the residual electrostatic charge image so that the toner particles adhere to the charged areas and form a visible image. In order to function properly for this purpose the toner must be capable of producing a colored layer of suitable density on the charged areas without unduly coloring the background areas.

In my above-identified application Ser. No. 597,247, I stated:

In liquid toners, a pigment is generally suspended in a carrier liquid, usually a hydrocarbon having a high electrical resistivity. Various pigments have been used, such as nigrosine and carbon black. In the preparation of toners for providing a black image, it has been difficult to simultaneously obtain uniform deposition over the image areas, otherwise known as "fill-in," consistent with dense black images which resist smearing when the dry copy is rubbed with fingers.

It is an object of this invention to provide a toner composition and a method for its production by which dense black and smear-resistant images may be formed in the electrophotographic process.

A further object is to provide a liquid toner which gives images having good fill-in.

Another object is to provide a liquid toner which has improved storage stability whereby suspension of the toner pigment in the carrier liquid is maintained and settling out of pigment in the toner liquid is minimized.

A further object is to provide a liquid toner composition and a method for making the composition whereby a controlled toner particle size is obtained.

These and other objects of my invention will become apparent as the description thereof proceeds.

I have now found that the above objects may be attained and an improved liquid for electrophotography produced by the use of my invention. In my invention the toner pigment is a finely divided carbon black dispersed in a hydrocarbon fluid containing a dissolved polymer together with a dye or pigment adsorbed on or associated with the carbon black, and a surface active agent.

The carbon black should be of particularly fine particle size, preferably not greater than about 25 millimicrons particle diameter as measured by electron microscopy. The carrier liquid is an odorless hydrocarbon liquid preferably Isopar G, an isoparafinic hydrocarbon fluid, manufactured by Humble Oil and Refining Co. The polymeric material, soluble in Isopar G, is preferably an acrylic polymer having a high degree of affinity for adsorption on the pigment, such as Neocryl B-707, manufactured by Polyvinyl Chemicals, Inc.

As surface active agents, I use solutions of metal salts of organic acids or mixture of such salts as they are often actually supplied or prepared during evaluation herein, the surface active agents being in a mineral spirits solution, such as,

6% cobalt tallate (Advance Div., Carlysle Chemical Works, New Brunswick, New Jersey)
6% manganese linoresinate (Harshaw Chemical Co., Cleveland, Ohio)
1.7% aluminum in aluminum Uversol liquid (Harshaw Chemical Co.)
6% manganese naphthenate (Advance Div., Carlysle Chemical Works)
6% cobalt naphthenate (Advance Div., Carlysle Chemical Works)
6% copper naphthenate (Advance Div., Carlysle Chemical Works)
4% calcium tallate (Advance Div., Carlysle Chemical Works)
6% manganese tallate (Advance Div., Carlysle Chemical Works)
6% copper oleate (Organics Div., Witco Chemical Co., New York, New York)
8% zinc tallate (Advance Div., Carlysle Chemical Works)
6% zirconium naphthenate (Zirco drier catalyst, Advance Div., Carlysle Chemical Works)
24% lead tallate (Advance Div., Carlysle Chemical Works)
6% iron naphthenate (Advance Div., Carlysle Chemical Works)
6% cobalt octoate (Advance Div., Carlysle Chemical Works)
5% calcium octoate (Advance Div., Carlysle Chemical Works)
4% rare earth naphthenate (Probably cerium and/or lanthanum, Advance Div., Carlysle Chemical Works)
8% copper tallate (Advance Div., Carlysle Chemical Works)
6% cobalt linoresinate (Harshaw Chemical Co.)
6% rare earth octoate (Advance Div., Carlysle Chemical Works)
4% calcium naphthenate (Advance Div., Carlysle Chemical Works)
5.6% cobalt Pastall (Harshaw Chemical Co.)
6% iron tallate (Advance Div., Carlysle Chemical Works)
6% manganese octoate (Advance Div., Carlysle Chemical Works)
28% tin octoate (Witco Chemical Co.)
8% zinc octoate (Advance Div., Carlysle Chemical Works)
8% copper octoate (Advance Div., Carlysle Chemical Works)
6% iron octoate (Advance Div., Carlysle Chemical Works)
24% lead octoate (Advance Div., Carlysle Chemical Works)
24% lead naphthenate (Advance Div., Carlysle Chemical Works)

8% zinc naphthenate (Advance Div., Carlysle Chemical Works)

as well as others too numerous to mention, and in admixture with one another.

In one embodiment of this invention the dye or pigment may be an alcohol- or water-soluble dye or may be soluble in some other solvent from which it may be deposited on the carbon black before evaporation of the solvent. It should be insoluble in the Isopar G or other carrier liquid.

In another embodiment the dye may be simply insoluble in Isopar G or other carrier liquid and may be admixed with the proper carbon black pigment so as to form a physical admixture rather than an adherent coating.

After presenting numerous illustrating examples, several of which are reproduced herein, I then stated in my copending application:

I have therefore found that a toner developer liquid which gives dense black smudge-resistant images in electrophotography and which does not settle out readily can be formed with a dispersion of very finely divided carbon black of the order of 20 millimicrons in a hydrocarbon carrier. Such carbon black particles have a natural tendency to form agglomerates and thus the agglomerated particles are present in the carrier liquid. It is necessary to control the size of the agglomerates since they will settle out in the liquid if they become too large. On the other hand, if the agglomerates are too highly dispersed the carbon black deposits on the latent electrostatic image as either individual particles or as much smaller agglomerates.

Individual carbon black particles, whether large or small, do not give dense black images. I believe that this is because light is simply reflected from the deposited individual particles causing the image to have a gray appearance. When the particles are large they also have a larger surface for light reflection. With the agglomerates, there is much open space between the agglomerated particles and much of the light striking the developed image is scattered internally in the agglomerates therefore giving a denser black appearance to the image.

The agglomerates remain in suspension due probably to the fact that they have a considerable amount of space between particles which contains lower-density carrier liquid and are therefore given reduced density per unit of agglomerate as compared to a single particle equal in size to the agglomerate in the carrier liquid.

Although larger particles can agglomerate to a limited extent they still present too much reflective surface and result in a gray image. Moreover, any agglomeration of large particles leads to settling out due to the higher specific gravity of large particle agglomerates.

In the fine-particle agglomerates, the agglomeration should be controlled by best image and best suspension-stability results, consistent with improved resistance of developed prints to smudging during handling operations.

The dispersion of the particles is aided by the presence of a certain amount of polymer in the carrier liquid, which polymer is soluble in the hydrocarbon carrier. I have found that an acrylic polymer in amounts between 5% and the limit of solubility of the polymer in Isopar G is excellent for this purpose when about 5% carbon black is used. Other polymers could be used either alone or in combination with this polymer and other ingredients to control agglomerate size, and their required quantities are determinable. Moreover, I have found that for proper dispersion, the carbon black should have a colorant such as a tinting dye, such as a basic triarylmethane dye or an alizarin water soluble dye or a pigment, adsorbed on or otherwise present with it. The amount of dye required is relatively small, being between about one to twenty six per cent by weight of the carbon black in the formulation present herein.

In order to maintain the agglomerates and not break them up into individual particles, the mixing of the toner concentrate into the carrier liquid for the final working toner should be by low-shear rate stirring and in such a manner that a high rate of shear is avoided. On the other hand, to prevent the agglomerates from becoming excessively large, a surface active agent should be present which is a metal salt of an organic acid.

Thus, by use of the aforesaid conditions and materials it is possible to obtain a toner developer liquid for development of latent electrostatic images which gives dense black, non-smudging images and has good suspension stability. Moreover, the images have a uniformly dense appearance regardless of difference in color on the original document. This is contrary to known toners which give images varying in density where the original document has varying colors in the image area.

In my application Ser. No. 597,240 I further stated:

The invention consists basically of developing a latent electrostatic image by means of a liquid toner, whereby the image is contacted both with a liquid toner containing very finely divided carbon particles or small agglomerates of them and with a liquid toner containing larger agglomerates of such particles. The development may be done in such a manner that the contact with each type of particle is in a separate step, in any order, or with a liquid toner which has a mixture of both types of particles. In my invention the toner pigment is a finely divided carbon black dispersed in a hydrocarbon fluid containing a dissolved polymer together with a dye or pigment absorbed on or associated with the carbon black and a surface active agent.

After presenting illustrative examples, several of which are reproduced herein, I then stated:

High relative humidity has been a problem in obtaining good prints in electrophotography. The present invention helps to solve this problem, which many investigators believe is caused by moisture adsorption on the paper and therefore is a problem to be solved by the paper manufacturer.

The proportions of ingredients used in preparing the toner composition are as follows:

In preparing a toner concentrate the amounts are based on the total weight of the concentrate. At least 0.01% of the colorant, i.e. a dye or pigment is used in conjunction with at least .01% carbon black with the upper limit depending on the viscosity limit for mixing. Isopar G is used up to 99% with the lower limit again determined by viscosity limit for good dispersion. The polymer is at least 0.1% with the upper limit being dependent on the solubility limit of the resin or the viscosity limit for good dispersion. Surfactant concentration for obtaining optimum prints will vary with each toner concentrate and it is within the skills of the art to determine the relative quantities of ingredients.

Working toners are prepared by diluting the toner concentrate with more Isopar G, in which a small quantity of additional surfactant may be dissolved. In actual commercial use the proportion of diluent is determined by the operator, but in many of these examples about 10 drops (about 0.5 ml.) of toner concentrate was added for each 100 ml. of Isopar G.

The ratio of the number of individual particles or small agglomerates to larger agglomerates is a matter of choice depending on the density of prints desired. A greater amount of finer particles gives prints with more gray appearance, whereas the greater amount of larger agglomerates gives a more black print.

Within the scope of my presently claimed invention the subject matter of my two earlier applications is supplemented and, in some cases, modified by a number of additional discoveries. Thus, for example, it is now believed that the most important functions of the previously described colorants, when added to the carbon black pigments, are to exert a protective colloid action on the carbon black and possibly to impart some change in the dielectric properties of the suspension, in addition to modifying the color of the carbon black images.

Moreover, a control of the electrical resistance of the toner concentrates or intensifiers and of their working toner dilutions within certain well-defined limits has been found to be of enormous practical importance. It has been found that this control can be established and maintained by a proper selection of the type and amount of the polyvalent metal soaps to be dissolved in the isoparaffinic hydrocarbon component of the toner.

Further improvements in copy quality have been made. Thus, toners producing even more intense black copies have been developed by utilizing minor proportions of certain blue pigments, notably Alkali Blue RS, in combination with major proportions of the dispersions of carbon black agglomerates described above, and novel red toners and blue toners are now provided.

My present invention therefore comprises the following principal features:

1. Methods of producing mill bases, toner concentrates and working toners, and the compositions so obtained, wherein a finely divided pigment is dispersed in a vehicle the essential ingredients of which are a hydrocarbon-soluble acrylic terpolymer resin of the type hereinafter described and a hydrocarbon-soluble polyvalent metal soap dissolved in a volatile isoparaffinic hydrocarbon of high electrical resistance, at least a part of the pigment being present as agglomerates the size of which is so controlled as to produce prins of high density by the combined action of the dissolved terpolymer resin and the dissolved metal soap.

2. Methods and compositions as described in (1) wherein the electrical resistivity of the isoparaffinic hydrocarbon is preadjusted, preferably by dissolving appropriate amounts of a polyvalent metal soap or a mixture of two or more metal soaps therein, to a value such that the resistivity of the vehicle is between about 1×10^9 and 1×10^{12} ohm-cm. when measured at 25°C.

3. Methods and compositions as described in (1) or (2) wherein the pigment is finely divided carbon black together with a minor proportion of a basic triarylmethane dye such as Victoria Blue B Base.

4. A method as described in (3) in which some of the carbon black agglomerates are partially broken down, as by the use of high frequency vibration, into smaller particles that provide good fill-in when the toner is used to develop an electrostatic image, and the toner concentrates and working toners so obtained.

5. Methods according to (1) to (4) wherein at least part of the metal soap is a manganese soap of a higher fatty acid, which soap has been solution-aged to a substantially constant electrical resistivity.

6. Toners according to (1) or (2) wherein the pigment is a blue pigment such as Alkali Blue RS or a cadmium red pigment such as Caddy Red Toner.

7. A method of obtaining a black toner capable of producing intense black prints, and the toner concentrates and toners so obtained, wherein a major proportion of a black toner of (3) to (5) above is blended with a minor proportion of the blue toner of (6), and

8. Selection of certain particular polyvalent metal soaps and certain combinations of soaps of two or more different polyvalent metals in order to obtain optimum:

a. preadjustment of the electrical resistivity of the isoparaffin to a value such that the vehicle will have a resistivity within the range of about 1×10^9 to 1×10^{12} ohm-cm. and preferably about 1×10^{10} to 5×10^{11} ohm-cm. at 25°C., and

b. maintenance of the proper size or sizes of agglomerates or agglomerate mixtures to obtain good image density and, if desired, good fill-in, consistent with stability upon standing, when used in combination with an acrylic terpolymer resin which is a terpolymer of vinyltoluene, a branched-chain butyl methacrylate and lauryl or stearyl methacrylate.

To the accomplishment of the objects and features set forth, and of others which will become apparent from the following description and claims, the invention consists in the provision of new toner concentrates and working toners and their methods of preparation and use, as is herein more fully described with reference to the accompanying drawing and pointed out in the appended claims.

Intensifiers And Working Toners

In electrostatic copiers of the type in which the toners of my invention are used, a toner concentrate, called an intensifier, is held in a supply receptacle and is metered into the toner tank by a measuring pump which delivers a predetermined volume of intensifier which is a function of the length of the original passing through the machine. The added intensifier is diluted to working strength both by the contents of the toner tank and by the addition of volatile hydrocarbon liquid or working toner to the toner tank.

The intensifier must therefore be able to retain its original composition throughout the supply bottle after prolonged standing in the supply bottle. Additionally, the working toner in the toner tank should retain its original composition throughout the lifetime of the tank contents. Settling and deposition of pigment from the intensifier is particularly harmful, since it causes pump clogging and also leads to reduced pigment input from the supply bottle to the toner tank. My present invention provides toner compositions that are storage-stable as mill bases and as concentrates or intensifiers, and which also possess stability after dilution to working strength toner, even when a part or all of their pigment content is in the form of flocculates or agglomerates imparting an improved hiding power.

The preferred materials to be used in practicing my invention are the following:

The pigments should be finely divided and highly dispersible in the vehicle used. Long flow channel carbon black pigments such as Mogul, Mogul Special, Mogul A and long flow furnace carbon black, Mogul L of the Cabot Corporation and the corresponding standard flow Peerless, long flow Peerless 155, and longer flow Peerless Mark II pigments of Columbian Carbon Company are preferred. Other carbon black grades can be used as well but do not yield equally good results. Suitable blue pigments are illustrated by Alkali Blue RS, a sulfonated triarylmethane dye, and by Cyan Blue GTNF. For red-colored prints a finely divided cadmium red pigment such as Caddy Red Toner, sold by the Industrial Chemicals Division of Allied Chemical Corporation, may be substituted for the black and blue pigments. In that event, Calcium Ten Cem solution has been found to serve well as the metal salt additive.

Victoria Blue B Base, (Color Index 44,045) a quaternary triarylmethane dye manufactured by the National Aniline Division of Allied Chemical Corp., is used as a suspending agent in admixture with the acrylic terpolymer and carbon black pigments. The Victoria Blue B Base is used in preparing black toners containing Neocryl B 707 polymer. In some as yet unexplained way, possibly related to either or both the protective colloid action, the adsorption of it or some of its ingredients on the carbon, or to its modification of dielectric properties, the Victoria Blue B Base modifies the Neocryl B 707 into a highly desirable material for toner preparation.

Alkali Blue RS is employed either as the sole pigment in blue toners or as a color-modifying agent in black toners. When used in admixture with carbon black pigments it assists in making a deep blue-black copy rather than the brown-black copy obtained without the alkali blue. It can be replaced by Cyan Blue GTNF, a quaternary diarylmethane dye which is described on page 1143 of "Synthetic Dyes" by Venkataraman.

The liquid vehicle of the toner is a solutuion of an acrylic copolymer resin and a polyvalent metal soap in an aliphatic hydrocarbon liquid which has a high but preferably carefully controlled electrical resistance. It possibly also contains some or all of the Victoria Blue B Base or some soluble ingredients leached from it. The preferred hydrocarbon is Isopar G, sold by Humble Oil and Refining Co. This is an isoparaffinic hydrocarbon fraction with a boiling range of 320°–350°F. Other isoparaffinic hydrocarbons with different volatility could be substituted. The preferred acrylic resin is a hydrocarbon-soluble copolymer of about 60 parts by weight of vinyltoluene, 20 parts of a branched-chain butyl methacrylate and about 20 parts of lauryl or stearyl methacrylate, described in U.S. Pat. No. 3,378,513 and sold as Neocryl B-707 by the Polyvinyl Chemical Co.

The polyvalent metal soaps are the hydrocarbon-soluble salts of organic acids. Representative compounds are listed above. The organic acids may be higher fatty acids of about 6–18 or more carbon atoms such as caproic acid, caprylic acid, 2-ethylhexoic acid, lauric acid, capric acid, myristic acid, palmitic acid, oleic acid or one of the commercially available higher fatty acid mixtures such as the tall oil fatty acids referred to above as tallates, or they may be naphthenic acids or linoresinic acids and the like.

The preferred polyvalent metal soaps for use in suspending carbon black pigments are the zinc, copper, cobalt, calcium, lead and manganese decylates, obtainable commercially from the Mooney Chemical Co. as the neutral zinc, copper, cobalt, calcium, lead and manganese neodecanoates under the trademark Ten Cems, the octoates of the same metals, and the rare earth metal soaps sold by Advance Division of Carlysle Chemical Works. Many other such metal salts of organic acids work well but are not preferred for other reasons such as odor, availability, poor light resistance, and so forth. The manganese soaps, upon dilution, should preferably be solution-aged in the manner hereinafter described. Calcium neodecanoate may be used to suspend Caddy Red Toner pigment and also to adjust the conductivity of the isoparaffinic hydrocarbon to the values hereinafter described. Any objectionable odor that may be caused by the presence of these metal soaps can be masked by dissolving a small amount of vanillin or other suitable hydrocarbon-soluble odor maskant in the Isopar G. Manganese soaps are particularly useful because of their ability to exert a stabilizing effect against oxidation of volatile isoparaffinic hydrocarbons.

The Liquid Vehicle

In my copending applications identified above I stated that the acrylic terpolymer resin improved the image density of prints made with carbon black toners containing it by forming agglomerates of controlled size containing finely divided carbon black particles in primary units and/or as aggregates of these units. The polyvalent metal soap becomes adsorbed onto these agglomerates and assists in suspending them in the hydrocarbon liquid and therefore the amounts used for this purpose are hereinafter sometimes described as suspending amounts. Suspension stability results from like positive charges imparted to the toner particles by adsorbed soap and/or terpolymer resin.

I have also found that there is a definite cooperation between the volatile isoparaffinic hydrocarbon fraction (Isopar G or its equivalent from other manufacturers) and certain polyvalent metal soaps, hereinafter sometimes called plateau type soaps, which are characterized by a high and approximately constant apparent equilibrium resistivity in the toners of my invention. Without the high resistivity the suspended agglomerates would quickly lose much of their positive electric charge. Without the approximately constant resistivity over a wide concentration range, the amount of polyvalent metal soap to be used would be within a severely limited range and would require extremely accurate control in formulating the intensifier and/or toner, for otherwise their suspension characteristics could vary materially from batch to batch. As will subsequently be explained in detail, the resistivity of the solutuion of polyvalent metal soap in Isopar G should fall within a range the outer limits of which are from about 1×10^9 to 1×10^{12} ohm-cm. at 25°C. and the preferred area of which is from about 1×10^{10} to about 5 to 10^{11}.

I have made resistance measurements on many of the polyvalent metal soap solutions of commerce, which are usually 5-8 percent metal content by weight solutions in mineral spirits. These were poured into a resistance cell with or without dilution with varying quantities of Isopar G and measured with and without aging.

Three distinct types of curves are generated when one plots the log of the resistivity of commercial metal soap solutions versus the log of their concentration in isoparaffinic hydrocarbon solution. The representative curves are plotted schematically in FIGS. 1–3 of the drawings.

In Type I behavior, shown in FIG. 1, the resistivity changes by at least a factor of 10 after a few days aging of the soap solution. The curve for the aged soap solution is seen to be nearly horizontal over a large range of concentrations at the lower end of the concentration scale. At higher concentrations, the resistivity drops more sharply with small changes in concentration. Manganese and rare earth metal soaps, for example, manganese octoate manganese Ten-Cem, and rare earth octoate are illustrative of this type of behavior.

In Type II behavior, shown in FIG. 2, the resistivity of both the aged and unaged soap solutions is similar to that of the aged soap solutions of Type I. The resistivity is a plateau and then drops sharply at higher soap concentrations. Aging has little or no effect on resistivity, and does not change the shape of the curve. Zinc, copper and lead octoates and Ten Cems exhibit this type of behavior.

The soaps of Type II and the aged soaps of Type I are therefore designated as plateau type soaps, because a large variation in soap concentration has little, if any, effect upon resistivity. They are of particular value as suspending agents for pigments and pigment agglomerates, as has been described above.

In Type III behavior, shown in FIG. 3, the resistivity drops steadily with increasing soap concentration. The slope of the curve is relatively constant, and there is no plateau as with the Type I and Type II soaps. Aging has little if any effect on their resistivity. Zirconium, calcium, cobalt and iron soaps, for example, the octoates and Ten Cems of these metals, exhibit this type of behavior. These and other metal soaps of the same resistivity characteristics are sometimes hereinafter defined as constant slope type soaps. They are particularly useful in adjusting the conductivity of the isoparaffinic hydrocarbon solvents in the manner hereinafter described.

Aged soap solutions of Type I and soap solutions of Type II, aged or unaged, clearly lend themselves toward the preparation of toner compositions whose resistivities fall within the desired range even when subjected to very large changes of concentration, such as, for example, considerable dilution with isoparaffinic hydrocarbon solvents.

The manganese soaps, which are of Type I are among the best surfactants for use in practicing my invention after they have been properly aged. Solutions of these soaps, and particularly the more highly dilute solutions used in preparing the toners of this invention, have an unusually great response to aging. The following test results with manganese octoate (manganese salt of 2-ethylhexoic acid) are illustrative. 1.6 grams of commercial 6% (by weight of Mn metal) manganese octoate solution was diluted with Isopar G to make 135 grams of solution. A sample of this solution was aged by standing in the resistivity cell at room temperature and the cell resistance as a function of time was measured. The test results are shown in Table I.

Table I

Age of Mn $(OOC.C_7H_{15})_2$ Soln. in Hours	Cell Resistance in Ohms
0	1.0×10^8
1.1	1.0×10^8
2.2	3.7×18^8
3.3	1.1×10^9
4.3	2.6×10^9
5.5	3.7×10^9
6.5	4.9×10^9
7.7	5.7×10^9
8.8	6.2×10^9
10.0	6.3×10^9
22.25	7.5×10^9
30.25	9.5×10^9
95.25	1.5×10^{10}

The chemical nature of the change that takes place on aging has not been determined, but the increase in electrical resistance is clearly seen. It is accompanied by a visible intensification of color. Constancy of conductivity with varying concentration suggests establishment of some equilibrium condition in the solutions which is lost at higher soap concentrations.

The zinc, copper, lead and solution-aged manganese neodecenoates and the solution-aged manganese and rare earch metal octoates are capable of producing toner intensifiers of good storage stability and working toners giving good-to-excellent copies on Interchemical Corporation LC-65 electrofax copy paper when used in quantities within the range of 0.4, 0.8, 1.2, 1.6 and 2.0 grams of the polyvalent metal soap for each 135 grams of total intensifier solution. It will be understood, however, that within this range the optimum quantity of polyvalent metal soap will vary with the type and quantity of carbon black, Victoria Blue B Base and Alkali Blue RS pigment composition in suspension and also with the quantity of acrylic terpolymer used. Moreover, if these ingredients are varied widely in concentration, the range can shift somewhat. Lead neodecanoate has the same desirable high electrical resistance over a wide range of concentrations, but does not give quite as good prints as do the other polyvalent metal soaps of the above-described group.

Zirconium soaps such as the commercial product Zirco, described in U.S. Pat. No. 2,739,905 as zirconium octoate, may likewise be employed by themselves and will produce good toners, but are more frequently used in conjunction with soaps of other metals, which are most advantageously plateau type soaps. In these mixtures the zirconium soaps function as resistivity-adjusting agents.

In the intensifiers and working toners, unaged solutions of the manganese soaps produce copy of good quality but have a higher degree of settling while still fresh because of their higher conductivity. The settling is worse in the more concentrated intensifiers than in the more dilute toners. This difficulty is overcome by aging their solutions to a constant electrical resistivity as described above.

The acrylic terpolymer is a major factor in producing pigment agglomerates of reasonably small controlled size which do not settle at an excessive rate. Optimum results are usually obtained when it is present in substantial amounts relative to the total pigment content. The amount of polymer can be varied within a range of from about 30 grams to about 200 grams for each 15 grams of pigments. This is sometimes hereinafter called

a dispersing amount. The quantity within this range should preferentially be about 10 times the weight of pigment. Thus, as will subsequently be described in greater detail, I have obtained toner concentrates of excellent storage stability that produce good prints upon dilution to working strength wherein the vehicle contains 120 grams of the terpolymer and from 0.7 to 3 grams of aged manganese octoate or neodecanoate in 210 grams of Isopar G for each 15 grams of long flow channel carbon black pigment containing about 0.4 percent of its weight of Victoria Blue B Base. Even larger quantities on the order of 160 grams of Neocryl B-707 in 210 grams of Isopar G may be used to advantage in suspending each 15 grams of an inorganic pigment such as Caddy Red Toner. In the aforementioned copending applications, significantly less polymer was employed with a different grade of carbon black than those described herein. As a result of changing the quantity of polymer and the nature of the carbon black, I have found that any metal salt surfactant described in the copending application can be made to give good or excellent copy when included at the proper concentration in a working toner prepared according to this present continuation-in-part. Similarly, admixtures of metal salts may be employed.

The Resistivity of the Volatile Isoparaffinic Hydrocarbons

I have found that volatile isoparaffinic hydrocarbon fractions of the type of Isopar G undergo substantial changes upon aging, and that these changes have an important effect on its behavior in the toner compositions of my invention.

These changes are most probably the result of oxidation that may occur during storage, or even as a result of minor variations in manufacture of the hydrocarbon fraction. They may be evidenced by a decrease in its resistivity from its original specification value, which corresponds to a resistivity at 25°C. of 1×10^{14} ohm-cm. or higher, and also in a modification of its behavior upon addition of certain polyvalent metal soaps.

The control of these factors is an important feature or the present invention. Preferred methods of obtaining this control are shown diagramatically on FIG. 4 of the drawings.

Referring to this Figure, Point R represents the resistivity of isoparaffinic hydrocarbon solutions of metal soaps at infinite dilution, i.e., at zero effective soap concentration. The resistivity represented by point R is a function of the particular batch of isoparaffinic hydrocarbon. Representative batches, depending on their time of storage have differed by as much as a factor of 100 in resistivity; the fresher batches being more resistive. The value of the resistivity R can be adjusted downward by the addition of a Type III soap, for example, zirconium octoate, as indicated by the line RD.

The shaded area AA' B' B represents a preferred range of resistivities for the toners of this invention. In order that the toners exhibit a resistivity plateau over a wide range of concentrations, one or more plateau type soaps (Type I or Type II) should be added to the solution of the Type III soap. The resistivity of the toners of this invention is substantially the same as the resistivity of a soap solution having the same soap concentration.

A plateau type soap added to the isoparaffinic hydrocarbon represented by point R generates a resistivity curve RE, which enters the preferred area only at relatively high soap concentrations and on its steep portion. However, if the resistivity of the isoparaffinic hydrocarbon is preadjusted downward, preferably within the desired range, to R' by the addition of a Type III soap up to concentration S, then the plateau-type soap may be added in quantities such that its plateau portion is within the preferred resistivity range as illustrated by curve R' E'.

By this procedure, toners having the preferred resistivity can be obtained from batches of isoparrafinic hydrocarbon regardless of whether their resistivity meets the minimum product specification value.

A wide range of amounts of Type I or II soap may be added to the solution of Type III soap within the range ABB'A' without materially affecting resistivity.

It should be noted that toner compositions prepared by addition of Type III soap alone along RD and within the shaded area function well as toners.

Any hydrocarbon-soluble polyvalent metal soap is capable of adjusting the initial conductivity of the hydrocarbon. However, there is an important practical advantage in using "constant slope" type soaps such as zirconium, calcium and the like, because these produce relatively uniform and rapid increases in conductivity upon addition to the hydrocarbon. Soaps of plateau-type metals such as zinc and manganese, on the other hand, produce irregular increases. Therefore manganese octoate, for example, may not generate sufficient conductivity in fresh Isopar G unless so much is added as to be on the steep part of the conductivity curve, where conductivity control is more difficult and there is danger of degradation of the toner.

Any soap that is used, either alone or in a combination with one or more others, should be capable of producing a toner that will make pleasing copies. There is a certain degree of specificity of ingredients for generating the best copy possible. For this reason, soaps should not be chosen solely for their ability to adjust conductivity, and it is an advantage of my invention that it provides a wide range and variety of soaps from which to choose.

Toner Preparation

In compounding toners in accordance with the invention a mill base is first prepared by milling together the pigment or pigment mixture and a portion of the vehicle. If manganese octoate or neodecenoate is to be used either alone or in combination with one or more other surfactants in the vehicle it may be dissolved in Isopar G or other volatile hydrocarbon and the solution aged for about 48 hours, or until its electrical resistance has become substantially constant at the proper level. If other surfactants, such as Zirco, are to be substituted the aging may not be needed. A water-cooled sand grinder of the type supplied by Chicago Boiler Co. is preferably used so that its contents can be kept at about 30°–35°C.

The optimum quantity of volatile hydrocarbon to use in preparing the mill base may vary with the type of pigment being used and also with the amount of acrylic copolymer resin being employed. However, it should in all cases be sufficient to dissolve all of the acrylic copolymer resin and polyvalent metal soap, and in general it should be about 5 to 20 times the weight of the pigment or pigments used.

The toner concentrate, or intensifier, is made by diluting the mill base with additional volatile hydrocarbon, the electrical resistivity of which has preferably seen adjusted to a value within the range of about 1×10^9 to 1×10^{12} ohm-cm. by the addition of a suitable polyvalent metal soap as previously described. The strength of the toner concentrate may vary widely, but in most of the representative cases the amount of additional hydrocarbon will be about ten to forty times the weight of the mill base.

The toner actually used, which is called the working toner, is made by further diluting the toner concentrate. This may be done by metering it into a receptacle that already contains a supply of working toner, usually with the simultaneous or subsequent addition of a suitable isoparaffinic diluent (such as Isopar G) or by the addition of working toner. Alternatively, a part or all of the Isopar G may be mixed directly with the toner concentrate to make the working toner.

The solids content of the working toner will vary between wide limits, and will in many cases be adjusted by the operator of the copying machine in accordance with such factors as the amount of pigment he wants to apply to the page, the density and other characteristics of the print desired, the background clarity desired, the type of paper being used, and the like. It is apparent, therefore, that no meaningful limits can be stated; conceivably such high dilutions could be used that the solids content of the working toner would be on the order of 0.0001% whereas working toners containing as much as 1% solids or more might sometimes be employed.

Long flow channel carbon black pigments of the type described above produce toners of good storage stability when used in the above-described liquid vehicles containing Victoria Blue B base and having a resistivity within the indicated range, but a neutral black color of the prints is created by substituting Alkali Blue RS pigment for part of the carbon black. Thus, for a neutral black toner a preferred pigment composition may contain about 2.5 to 3.5 grams of Alkali Blue in uniform admixture with 12.5 to 11.5 grams of carbon black. On the other hand, as is shown in Example 2, the pigment may consist entirely of Alkali Blue when dense blue prints are desired. Similarly, red pigments such as Caddy Red Toner R 6222 may be used to obtain red prints. Cyan Blue GTNF may be substituted for part or all of the Alkali Blue RS. Victoria Blue B base should preferably be present in all pigment compositions containing both a carbon black pigment and an acrylic terpolymer resin such as Neocryl B 707 because of its suspending action, as has been pointed out above. These materials are preferably dispersed in a sand mill, although it will be understood that other dispersion equipment may be employed.

Preliminary tests are made on the volatile isoparaffinic hydrocarbon solvent (Isopar G or its equivalent) to determine its electrical resistivity. This is usually done by conductivity measurements. Direct current resistance measurements in this range are feasible if a very low voltage is applied across the measuring cell to avoid polarization. The resistivity is then preferably adjusted to the optimum value described above most frequently in the range of 1×10^{10} to 1×10^{12} ohm-cm. by adding a sufficient amount of a hydrocarbon-soluble zirconium compound such as zirconium octoate or decylate or another oil-soluble polyvalent metal soap such as those described above as being suitable. It is advisable to do this with each new batch of hydrocarbon solvent, and it may also be done at any stage in the dilution procedure where resistance control is necessary or desirable. The acrylic copolymer resin may be dissolved directly in the hydrocarbon solvent so adjusted, but it may also be added to the mill in solid form with the proper amount of zirconium or other soap being added later.

The invention will be further described and illustrated by the following specific examples, which set forth preferred embodiments thereof. It will be understood that in these examples:

1. In all references to metal soaps in solution, except where a different meaning is expressly stated, the percentages refer to the percent metal in solution. Thus 6% manganese octoate contains 6% of manganese by weight, this manganese being present as the octoate, or 37.2 percent solids.

2. Examples 1–7 and Example 18 include and illustrate the additional subject matter of the present application. In each of these examples the electric resistivity of the Isopar G has been adjusted, by the procedures described above, to a value such that the resistivity of the toner vehicle is within a range between about 1×10^9 and 1×10^{12} ohm-cm. at 25°C. and is usually (and practically always in those toners which contain flocculates of carbon black pigments) between about 1×10^{10} and 1×10^{12}. Examples 8–17 are taken from my copending applications referred to above.

3. In the working toners the proportion of Isopar G to the solid ingredients is not critical. Although preferred quantities or ratios are sometimes given, it is within the province of the operator to adjust the concentration or solids content of either the intensifier or the working toner, or both, by increasing or reducing their content of volatile hydrocarbon as has been described above. The term "solvent quantities" will therefore sometimes be used to state the amounts of this ingredient in the compositions of the invention.

4. The terms "agglomerates" and "flocculates" are used interchangeably, both in the foregoing specification and in the examples and claims, to express the results obtained by the coming together of smaller particles which may or may not have been previously dispersed, regardless of the usage of these terms in other fields.

EXAMPLE 1

Brown-Black Toner

A brownish-black toner and intensifier suitable for use in a Pitney-Bowes Model 250 copier whose pump-activating cam is adjusted to deliver 0.4 ml. of intensifier per pump cycle is prepared as follows:

The sand grinder is charged with:

14.4 grams of Mogul Special Carbon Black
0.6 grams of Victoria Blue B Base
185 grams of a solution, previously aged for 2 days, which was prepared by dissolving 9.07 grams of 6% manganese octoate solution in 2,000 ml. (1496 grams) of Isopar G
896 grams of Ottawa sand

The mill is operated for about 30 seconds to disperse the pigments in the Isopar G. Then a total of 120 grams of Neocryl B-707 in free-flowing bead form is added in a few seconds to the mill while agitation proceeds. Cooling of the mill container is accomplished by pass-

ing water through it at a rate sufficient to maintain 30°–35°C. in the agitated mass. Milling is continued for approximately 15 minutes after the last of the Neocryl B-707 has been added, after which the mill base is separated from the sand by screening. It contains about 43% solids.

The intensifier, or toner concentrate, is made by dispersing mill base in additional Isopar G hydrocarbon having one or more of the above-described polyvalent metal soaps dissolved therein. If the soap is manganese octoate or decylate its solution in the Isopar G should be aged at least two days before addition of the mill base. In a typical example, 17 grams of the abovedescribed mill base are added to 153 grams of a solution prepared by dissolving 27.2 grams of the 6% manganese octoate solution in 2,000 ml. of Isopar G and aging for two days to bring the resistivity to the range of 1×10^{10} to 5×10^{11} ohm-cm. The ingredients are mixed in a Waring Blendor for one minute at line voltage. The resulting toner concentrate contains about 5 percent solids.

A working toner is made by dissolving 2.55 grams of the 6% manganese octoate solution in 2,250 grams of Isopar G, aging 48 hours, adding 187 grams of the intensifier and agitating for one minute in a Waring Blendor whose input voltage is 70 volts. This toner produces very dense brown-black copies of half-tone originals. It contains about 0.4% solids. Because of this high pigment concentration, background density is not as low as is desired. Further dilution with Isopar G produces excellent copies with lower background level.

In the above example, manganese octoate was introduced into the products at each stage of the dissolution or dilution procedure. In fact, it can be introduced in one or more of the steps as is illustrated below.

EXAMPLE 2

Blue Toner

Mill base preparation. The sand mill is charged as in Example 1 with:

15 grams of Alkali Blue RS
120 grams of "Neocryl B-707
185 grams of Isopar G

and is operated for 15 minutes with the contents at about 33°C.

Intensifier preparation: A solution of 27.2 grams of 6% manganese octoate in 2,000 ml. of Isopar G is aged 48 hours. Then, 17.0 grams of the mill base are dispersed in 153 grams of this solution in a one quart Waring Blendor at full line voltage.

Working toner preparation: 93.75 grams of the intensifier is dispersed in 2,250 grams of Isopar G in a 1 gallon Waring Blendor at "low" speed setting with a line voltage of 70 volts.

This toner produced dense blue positive images. Their appearance was marginally, if at all improved when 0.5 grams of the Alkali Blue RS in the above formulation was replaced by an equal quantity of Victoria Blue B Base.

EXAMPLE 3

Toner Mixture

Another important embodiment of my present invention comprises the mixing together of two separately prepared toners, toner concentrates or mill bases in order to obtain compositions which have the optimum color, density and storage suspension. This method can be used to select the best carbon black pigment and tinting dye and their optimum ratio for mixing by compounding those compositions of each, taken separately, which have the best nonsettling characteristics, and then preparing blends of various proportions of these compositions to get the desired color and density.

Mixtures of the working toners of Examples 1 and 2 were prepared in this manner. The blue toner of Example 2 had approximately double the pigment concentration of the brown-black toner of Example 1. Mixtures ranging from 86% to 94% by weight of the toner of Example 1 with 14% to 6% of the blue toner of Example 2 were prepared and were found to produce, when the percentages of ingredients were varied in the order stated, copies that ranged from bluish-black to brownish-black in shade. A very pleasing neutral shade of black was obtained by mixing about 10% of the double strength blue toner with about 90% of the single strength brown-black toner.

The Victoria Blue B Base was not effective as a shading agent in these toners. Its color was found to be variable between brown and blue in different batches. Moreover, while its presence in making satisfactory black toners was required, I was able to use it in very small amounts such as 0.1 gm Victoria Blue B Base plus 14.9 gm Mogul Special. Even when used as 1.2 gm Victoria Blue B Base plus 13.8 gm Mogul Special, no evidence of improving the shading of the brown-black images was obtained.

EXAMPLE 4

Red Toner

The principles of the invention are also applicable to toners which contain a red pigment instead of carbon black. Thus a liquid developer of good stability which produced red copies was prepared as follows:

Mill base preparation: A sand mill was charged with
896 grams of sand
15 grams of Caddy Red Toner R 6222 (Allied Chem. Corp.)
210 grams of Isopar G

The mill was started and 160 grams of Neocryl B-707 were added. The mixture was then milled for 15 minutes while maintaining the contents at a temperature of about 33°C. after which the mill base concentrate was separated from the sand by sieving.

Intensifier preparation: A solution of 0.375 grams of 6% calcium neodecanoate, available commercially as Calcium Ten Cem, diluted with Isopar G to 135 grams of solution was prepared. To this there was added 4.97 grams of the Mill Base with one minute agitation in a one quart Waring Blendor at line voltage. A composition containing 0.17% solids and having excellent storage stability was obtained.

Working Toner preparation: This was made by adding 150 grams of the Intensifier to 1350 grams of Isopar G in a one gallon Waring Blendor at 70 volts line voltage. When used in a Pitney-Bowes Model 250 Electrostatic Copier it produced red prints having good density, sharp edges and clean background.

EXAMPLE 5

Black Toner

A composition for producing black copies on a clean white background from line copy originals in the Pit-

ney-Bowes 250 copier is prepared by the procedure described below.

The Pitney-Bowes Model 250 Copier contains a toner tank which is kept at an almost constant level by gravity feed from an inverted bottle of liquid. The main means of supplying the solid particulate matter component of the toner to the tank during the process of preparing copies (which remove particulate matter from the tank) is to operate a pump which delivers a metered amount of an "intensifier" (which is a more-concentrated version of the "working toner" contained in the toner tank) into the tank for each rotation of a cam in the copier. The cam rotates once per prescribed interval of length of copy paper which passes through a pair of rollers geared to the cam. By means of levers the cam is actuated approximately once for each 11 inch original document fed into the machine, since the motion of the copypaper is directly proportional to the motion of the original document. The pump stroke per cycle may be controlled by means of a knurled thumbscrew which determines at which height on the cam the pump stroke is initiated. The pump specification calls for delivery or a maximum of 0.7 ml per cycle and is adjustable for smaller volumes by means of the thumbscrew. The pump delivery setting is made for a particular intensifier. If an intensifier having a significantly different concentration of pigment is used to replace an intensifier for which the pump stroke has been properly adjusted, then a pump stroke adjustment must be made. The intensifier concentration is arrived at by trial and error. First, the pump stroke is adjusted to a preselected value. Then, the intensifier is installed in the copier and many thousand copies of an "average" original are made. If the intensifier is too concentrated, these copies will gradually darken. If it is too dilute, they will gradually lighten up. At the proper concentration, copy density as judged visually, remains unchanged for many thousand copies.

An average original is hard to define. Obviously, if too much image area is on the original, the toner will be depleted too rapidly, and vice versa. I have found that a typewritten 8½ × 11 inch original containing ⅔ of a page of printing, single spaced, with 1 inch to 1¼ inch margins is a suitable average original. Intensifiers in several field test Pitney-Bowes Model 250 Copiers performed well with many thousand copies being made from random originals after the intensifier concentration had been arrived at by trial and error using the average original.

In Example 3 a black toner was prepared by mixing a brown-black toner with a blue toner. In the present example the pigments are mixed to achieve the same result. The procedure is as follows.

Mill Base

11.79 gram Mogul Special Carbon Black
0.49 gram Victoria Blue B Base
2.72 gram Alkali Blue RS
160 gram Neocryl B-707
210 gram Isopar G

This mixture is ground with 896 grams of sand in the sand mill for 15 minutes with the contents maintained at 33°–37°C.

Intensifiers and Working Toners

a. For use when the pump of the intensifier tank is set to deliver 0.7 ml. per stroke.

Prepare an intensifier by dissolving 1.6 grams of 6% manganese octoate solution in 133.4 grams of Isopar G and aging the solution for two days. Then add 4.97 grams of the Mill Base and mix for one minute in a one quart Waring Blendor at full line voltage (115 v.). Then age for at least 24 hours and again mix.

A working toner is made by adding 150 grams of the intensifier to 1350 grams of Isopar G, mixing for one minute at 70 volts line voltage on low speed in a one gallon Waring Blendor, aging for 24 hours and again blending.

b. For use when the intensifier tank pump is set at 0.4 ml. per stroke.

Prepare an intensifier by dissolving 3.5 grams of 6% manganese octoate solution in 131.5 grams of Isopar G and aging the solution for two days. Then add 8.70 grams of the Mill Base and mix one minute in a one quart Waring Blendor at full line voltage (115 v.). Then age for at least 24 hours and again blend.

A working toner is made by adding 90 grams of the intensifier to 1350 grams of Isopar G, mixing for one minute at 70 volts line voltage on low speed in a one gallon Waring Blendor, aging for 24 hours and again blending.

For use with originals containing half-tone photographs and wider line copy, the same intensifiers may be used in twice the amounts sppecified above to make working toners: i.e., 300 grams and 180 grams respectively. Users prefer a more concentrated working toner when copying originals of this type than when the originals are typed matter or narrow-line graphics.

EXAMPLE 6

Black Toner

In the Pitney-Bowes Model 252 copier a measured quantity of working toner is first poured into the toner tank and a more concentrated replenisher is added as desired by the operator. Alternatively, the toner may be made directly in the toner tank. The Mill Base in this example may serve as a replenisher and is prepared by charging the sand mill with:

896 grams of Ottawa sand
11.79 grams of Mogul Special Carbon Black
0.49 grams of Victoria Blue B Base
2.72 grams of Alkali Blue RS
160 grams of Neocryl B-707
54.5 grams of 6% manganese octoate in mineral spirits dissolved in 155.5 grams of Isopar G

All of these ingredients are milled together at 33°–37°C. for 15 minutes. The liquid is separated from the sand and added to 1760 ml of Isopar G in the toner tank with stirring and in small increments to generate a working toner which gives satisfactory positive images which improve in quality as the working toner ages for a day or two.

Alternatively, a less viscous mill base replenisher which makes excellent copies immediately upon dilution to working toner composition may be made by substituting the proper amount of Zirco for the manganese octoate used herein. The proper amount of Zirco included in the mill base is that which brings the working toner conductivity into the preferred range as cited above when the mill base is diluted with Isopar G to make the working toner.

EXAMPLE 8

Working toner compositions were prepared using for

each composition the combination of ingredients listed below and one surface active agent from the above list in the quantities stated.

The toner concentrate dispersion was prepared from the following ingredients:

75 gm Neocryl B-707 (Lot No. 21062-an acrylic polymer manufactured by Polyvinyl Chemicals, Inc., Peabody, Mass.)

210 gm Isopar G (Humble Oil and Refining Co., Inc., Pelham, N.Y.)

15 gm Monarch 74 carbon black (manufactured by Cabot Corp., Cambridge, Mass. average particle size 17 millimicrons by electron microscopy and containing 4% by weight of Victoria Blue B Base, a triarylmethane dye manufactured by the National Aniline Division of Allied Chemical Corp., deposited from a methanol solution by agitating in a Waring Blendor for 10 minutes, dried overnight at 50°C., then for 1 hour at 110°C., cooled and micropulverized in air)

by mixing the ingredients and milling them in a sand mill (Model L-1, Chicago Boiler Co., Chicago, Ill.) for 15 minutes without cooling. Shorter times are also satisfactory for the pigment dispersion operation. The toner concentrate dispersion was then separated from the sand by sieving. The concentrate was agitated by high frequency vibration for 5 minutes using a Model A Branson Sonifier ultrasonic generator, and cooled to room temperature.

A separate batch of woking toner was made by stirring 1 drop of surface active agent solution into 100 ml. Isopar G and then adding 10 drops (about 0.5 ml.) of toner concentrate dispersion to the Isopar solution with stirring.

Each batch of working toner was then agitated ultrasonically using the Sonifier for one minute before use.

Latent electrostatic images were prepared by charging and exposure in a Pitney-Bowes Model 250 Photocopy Machine on zinc oxide-coated sheets of electrostatic copy paper from a supply roll (Interchemical Corp. paper No. LC-20), and developed one at a time by each of the working toners in turn. The working toner was slowly poured over the exposed sheet in a darkroom.

Developed copies were obtained with the following polyvalent metal soaps:

Copper, cobalt and calcium oleates.

Calcium, zinc, copper, cobalt, manganese, lead and iron tallates.

Manganese, iron and cobalt linoresinates.

Aluminum Uversol liquid.

Calcium, zirconium, copper, cobalt, manganese and rare earth naphthenates.

Manganese octoate.

EXAMPLE 9

In this example, a working toner was prepared according to Example 8 and containing cobalt linoresinate except that the high frequency agitation of concentrate and working toner were varied as shown in Table III.

Table III

	Concentrate		Working Toner	State of Dispersion
(1)	No ultrasonic agitation	(A)	No ultrasonic agitation	Large agglomerates
(2)	No ultrasonic agitation	(B)	Ultrasonic agitation, 1 minute	Ultimate particles or small agglomerates
(3)	Ultrasonic agitation, 5 minutes	(C)	No ultrasonic agitation	Large agglomerates
(4)	Ultrasonic agitation, 5 minutes	(D)	Ultrasonic agitation, 1 minute	Ultimate particles or small agglomerates

Electrostatic latent images were developed using each of the four working toners, (A) – (D).

The cobalt linoresinate concentration was varied in each of the four working toners as follows: 0, 1/6, ⅛, ¼, ½, 1, 2, 4, 8, 16 drops of cobalt linoresinate solution per 100 ml of working toner. There was approximately 20 drops of this solution in 1 ml.

The change of concentration of the cobalt linoresinate had no effect on background density in the developed images but did produce significant changes in image density.

High frequency agitation of both the concentrate and the working toner as in (D) gave the greatest degree of pigment dispersion, best fill-in, best tail-off elimination, but not the highest image density. Also, the background density was highest. Tail-off refers to streaking caused by agglomerates breaking up after deposition on the latent image.

Maximum image density with low background was obtained with toners (A) and (C). The working toners (A) and (C) were prepared by dropwise addition and simple low-shear-rate stirring of the concentrate into the solution of surfactant in the carrier liquid Isopar G. Thus these working toners were not submitted to the high shearing forces produced by ultrasonic agitation.

Toners (B) and (D) gave good fill-in and had excellent dispersion but moderate background density. However, when a working toner was prepared with ultrasonic agitation of both concentrate and working toner as in (D), but omitting the cobalt linoresinate surfactant, the dispersion was very poor and the rate of sedimentation was rapid, complete settling occurring overnight. This ability of ultrasonic agitation to either produce or retard agglomeration in the absence or presence of additives, respectively, is not unexpected by those experienced in dispersion phenomena studies.

EXAMPLE 10

This example illustrates the effects of the agglomerate size of the carbon black under varying humidity conditions.

Developed prints of latent electrostatic images were made both at 55% relative humidity and 71% relative humidity as folllows:

a. Using interchemical electrostatic photoconductive paper No. LC-20, latent electrostatic images were made of an original document in a Pitney-Bowes Model 250 Photocopy Machine. The relative humidity was measured at 55%.

Toner liquid (D) of Example 9, where both concentrate and working toner were ultrasonically agitated, was used to develop an image. The same was done using toner (B) in which only the working toner was agitated ultrasonically.

Similar latent images were made and the same toners were used to develop the latent electrostatic images when the relative humidity measured 71%.

The density of the prints made and developed at 71% humidity were much less than the prints made and developed at 55% humidity showing that the highly dispersed toner liquids containing finer particles or smaller agglomerates did not develop as well at high humidity but did develop well at lower humidity.

b. Latent electrostatic images were made and developed at 55% humidity as in a) with the developing being done by the toner liquids (A) and (C) of Example 9, where the working toner was not ultrasonically agitated althrough the concentrate was in the case of (C).

In a similar manner, prints were made when the humidity measured 71%.

The prints made at the high 71% humidity had greater image density consistent with lower background density than those made at the lower 55% humidity. This demonstrates that the toner liquids containing agglomerates of small pigment particles developed well at high humidity and not as well at lower humidity. These prints had poorer fill-in than those developed with working toner which had been agitated ultrasonically.

EXAMPLE 11

Latent electrostatic images were made as in Example 10 at both 55% and 71% relative humidity and developed as described below.

The latent electrostatic images were treated both with liquid developer (C) and liquid developer (D) made as described in Example 9.

a. A latent electrostatic image was treated first with the developer liquid (C) and then given a second treatment with the developer liquid (D), both in complete darkness.

b. A latent electrostatic image was first treated with developer liquid (D) and then given a second treatment with developer liquid (C).

c. Developer liquids (C) and (D) were mixed together and a latent electrostatic image was developed with the resulting toner liquid.

In all instances (a), (b), and (c), the developed images were good and (a) and (c) had higher, almost equal density at both 55% and 71% relative humidity. They had a combination of high density and good fill-in. Images from (b) had good fill-in but slightly lower density.

This demonstrates that a toner which is less sensitive to change in humidity may be made by having present in the toner liquid both finely divided particles or small agglomerates of them along with larger agglomerates. Moreover, a method for developing over a wide humidity range is provided by developing in the presence of both types of particles, simultaneously or sequentially.

EXAMPLE 12

Working toners were prepared in accordance with Example 8 using the following ingredients:

50 gm Neocryl B-707 (Lot No. 21062)
235 gm Isopar G
15 gm dyed Sterling FT carbon black (Manufactured by Cabot Corporation, average particle size 180 millimicrons by electron microscopy and dyed with 3% by weight Victoria Blue B Base from methanol solution, ball milled 24 hours, dried and micropulverized)

sand milling for 15 minutes, separating and cooling the concentrate to room temperature. The concentrate was agitated ultrasonically for 5 minutes and again cooled to ambient temperature.

Working toners were made with 100 ml portions of Isopar G each containing 1 drop of cobalt linoresinate solution with the following amounts of toner concentrate added thereto: 10, 20, 30, 50 and 60 drops. Additionally, 1, 6 and 12 drops of cobalt linoresinate solution were used with 60 drops of toner concentrate. The working toners were agitated ultrasonically for 2 minutes.

Electrostatic latent images were developed with these toners. The images were generally gray with good fill-in and compared favorably with images developed with toner liquids manufactured by Interchemical Co., Inc. and Ditto, Inc.

Dispersion was not as complete as when the more finely divided Monarch 74 carbon black was used, as in Example 8.

When the concentrate was increased between 10 and 60 drops per 100 ml. Isopar G, there was no color shift in developed images. They were more dense but they were still gray.

Thus large particle size carbon black does not give the desired dense black images, even at relatively large pigment loadings per unit volume of working toner.

EXAMPLE 13

The following concentrate was prepared by sand grinding for 15 minutes and cooling to room temperature.

50 gm Neocryl B-707
235 gm Isopar G
14.4 gm Monarch 74
0.6 gm Victoria Blue B Base

This mixture was agitated ultrasonically for 5 minutes and cooled to ambient after which 10 drops were added to making working toners from 0, 1/256, 1/128, 1/64, 1/32, 1/16, ⅛, ¼, ½, 1, 2, 4, 8, and 16 drops cobalt linoresinate solution dissolved in 100 ml Isopar G. The optimum amount of cobalt linoresinate solution was found to be about 1/16 drop, with all working toners agitated ultrasonically for 1 minute.

Prints were made having different working toner treatment histories as follows:

a. Concentrate and working toner both dispersed ultrasonically.

b. Working toner only dispersed ultrasoncially.

c. Concentrate ultrasonically dispersed, working toner stirred manually.

Samples (a) and (b) contained smaller agglomerates and/or small individual particles and gave grayer prints having better fill-in.

Sample (c) contained larger agglomerates of small particles which produced dense black prints but with poorer fill-in than (a) or (b). Prints obtained from Sample (c) also had lower background density.

The same procedure was repeated using the following toner ingredients:

50 gm Neocryl B-707
235 gm Isopar G
12.5 gm Monarch 74
2.5 gm Milori Blue 15-1750 dye (a ferric ferrocyanide dye made by American Cyanamid Company)

The results in developing latent electrostatic images were the same as before in the present example except that optimum prints were obtained at 2 drops of cobalt linoresinate.

EXAMPLE 14

A toner was prepared as in Example 13b using the following ingredients:

30 gm Neocryl B-707
235 gm Isopar G
14.4 gm Monarch 74
0.6 gm Victoria Blue B Base

Results obtained were the same as in Example 13 with optimum prints being obtained at approximately 1/16 drop concentration of cobalt linoresinate solution. Moreover, excellent results were obtained when the surfactant was a mixture of 1/32 drop manganese linoresinate solution and 1/16 drop cobalt tallate solution.

Ultrasonic agitation of the above toner gave prints of almost the same density as a 1:1 mixture of a fine-particle toner and one prepared so as to contain agglomerates, indicating that the particles were reforming into agglomerates after the agitation was halted. This further indicates that the lower desirable limit of resin for controlling agglomeration is being approached and that the resin is active in controlling the agglomeration.

EXAMPLE 15

A toner concentrate was prepared by sand milling the following ingredients:

15 gm Neocryl B-707 (Lot No. 21062)
270 gm Isopar G
15 gm dyed Monarch 74 (dyed with 4% by weight Victoria Blue B Base)

for 15 minutes, separating and cooling the concentrate. The concentrate has a lower concentration of polymer than in Examples 8 and 14.

Working toners were prepared from 100 ml of Isopar G with varying amounts of cobalt linoresinate solution added thereto as follows: 0, 1/16, ⅛, ¼, ½, 1, 2, 4, 8, 16 drops and then 10 drops of the concentrate with stirring. The working toner was not ultrasonically agitated.

Latent electrostatic images were developed which showed poor pigment dispersion. The working toners settled out within one day, apparently because of the insufficient resin concentration for adequate pigment dispersion which produced such large agglomerates that pigment suspension was not stable for any appreciable length of time.

EXAMPLE 16

This example shows that a decrease in the concentration of Victoria Blue B Base in the concentrate creates a required increase in the amount of cobalt linoresinate to get the optimum print. The following concentrations were each sand milled for 15 minutes, cooled to ambient, agitated ultrasonically for 5 minutes, and cooled again to room temperature:

A 50 gm Neocryl B-707
235 gm Isopar G
14.85 gm Monarch 74
0.15 gm Victoria Blue B Base

B 50 gm Neocryl B-707
235 gm Isopar G
14.4 gm Monarch 74
0.6 gm Victoria Blue B Base

Toners were made from 10 drops of each of the above added to 100 ml Isopar G containing 0, 1/256, 1/128, 1/64, 1/32, 1/16, ⅛, ¼, ½, 1, 2, 4, 8 and 16 drops cobalt linoresinate solutions with ultrasonic agitation for 1 minute. Optimum prints were obtained at about 1 drop cobalt linoresinate in the working toner prepared from concentrate A and about 1/16 drop linoresinate for the working toner prepared from concentrate B.

EXAMPLE 17

Working toners were prepared from the following concentrate:

50 gm Neocryl B-707
235 gm Isopar G
15.0 gm Monarch 74

The prints obtained at all cobalt linoresinate concentrations were poor in this example involving the omission of Victoria Blue B Base. The dye is therefore acting in some way as a surface active agent, protective colloid, or the like, in improving the suspending power of the other toner ingredients on the Monarch 74. The basic nature of the dye as contrasted to the acid surface of Monarch 74 carbon black may be responsible, as may be the presence of aromatic groups in the dye molecule which might tend to be adsorbed on the carbon black surface.

EXAMPLE 18

Controlling Resistivity of the Vehicle

Mill base preparation: The sane grinder was charged with:

12.0663 gm Mogul Special Carbon Black
0.15 gm Victoria Blue B Base
2.7835 gm Alkali Blue RS
160 gm Neocryl B-707
210 gm fresh Isopar G
896 gm sand

and operated for 15 minutes at 33°C. The resulting mill base was separated from the sand.

Intensifier preparation: The resistivity of the Isopar G was measured and was greater than 1×10^{14} ohm-cm. To 134.2 grams of this isoparaffinic hydrocarbon there was added 0.8 grams of 6% Zirco dryer. The resistivity of the resulting solution was 3.6×10^{11} ohm-cm. There was then added 1.8 grams of manganese octoate, whereupon the resistivity of the solution was found to be 1.62×10^{11} ohm-cm.

The intensifier was made by mixing 135 grams of this soap-modified Isopar G with 4.97 grams of the above mill base in a one quart Waring Blendor for 1 minute at 115 volts. Its resistivity was then about 1×10^{11} ohm-cm.

Working toner preparation: To 1350 grams of Isopar G in a one gallon Waring Blendor there was added 150 grams of the above intensifier followed by agitation for 1 minute at 70 volts medium speed. The resistivity of the resulting toner was 8.8×10^{10} ohm-cm.

This toner had good suspension stability whereas intensifiers and toners from which the Zirco was omitted,

but which were otherwise the same, gave poorer prints and considerably less suspension stability.

What I claim is:

1. A liquid toner composition for use in electrophotography comprising a dispersion of about 15 parts by weight of finely divided pigment in a vehicle containing about 30 to 200 parts by weight of a hydrocarbon-soluble acrylic copolymer resin and about 0.01 to 3 parts of a hydrocarbon-soluble polyvalent metal soap both dissolved in a volatile isoparaffinic hydrocarbon the electrical resistivity of which is preadjusted to a value such that the resistivity of the vehicle is between about 1×10^9 and 1×10^{12} ohm-cm. when measured at 25°C., said acrylic copolymer resin being a terpolymer of vinyltoluene, a branched-chain butyl methacrylate and lauryl or stearyl methacrylate, said pigment consisting essentially of finely divided carbon black particles whose diameters are not greater than 25 millimicrons associated with a hydrocarbon-insoluble dye of the group consisting of basic triarylmethane dyes and alizarin dyes, at least some of said carbon black being present in the form of agglomerates of said particles of carbon black, said agglomerates being of a size that will produce high density upon development of an electrostatic image with said composition, and said polyvalent metal soap being a member of the group consisting of the zinc, iron, copper, lead calcium, zirconium and solution-aged rare earth metal and manganese soaps of fatty acids of about 6–18 carbon atoms and mixtures thereof.

2. A liquid toner composition according to claim 1 wherein a part of the carbon black is present in the form of agglomerates of a size as defined in that claim and the remainder of the carbon black is present in a form of particle association having a size smaller than said agglomerates and of a size that will produce good fill-in upon development of an electrostatic image with said composition.

3. A liquid toner composition according to claim 1 which comprises a suspension of about 15 parts by weight of a finely divided carbon black-Victoria Blue B Base (Color Index 44045) pigment mixture in a vehicle containing about 30 to 200 parts by weight of a hydrocarbon-soluble acrylic copolymer resin and a suspending quantity of a hydrocarbon-soluble polyvalent metal soap both dissolved in a volatile isoparaffinic hydrocarbon preadjusted to an electrical resistivity such that the resistivity of the vehicle is between about 1×10^{10} and 5×10^{11} ohm-cm. when measured at 25°C., at least a part of said pigment mixture being in the form of agglomerates of increased hiding power.

4. A liquid toner composition according to claim 3 wherein the pigment contains a major proportion of finely divided long flow carbon black together with minor quantities of Alkali Blue RS and Victoria Blue B Base (Color Index 44045) pigments.

5. A liquid toner composition according to claim 1 which comprises a suspension of about 15 parts by weight of a carbon black-Victoria Blue B Base (Color Index 44045) pigment mixture in a vehicle containing about 30 to 200 parts by weight of a hydrocarbon-soluble acrylic copolymer resin and a suspending quantity of a hydrocarbon-soluble polyvalent metal soap both dissolved in a volatile isoparaffinic hydrocarbon preadjusted by the addition of a member of the group consisting of hydrocarbon-soluble zirconium, calcium and cobalt soaps and mixtures thereof to an electrical resistivity such that the resistivity of the vehicle is between about 1×10^{10} and 5×10^{11} ohm-cm. when measured at 25°C., at least a part of said pigment mixture being in the form of agglomerates of increased hiding power.

6. A method of preparing a toner for use in electrophotography and capable of converting a latent electrostatic image into a print having both high image density and good fill-in which comprises

a. Dispersing about 15 parts by weight of a mixture of finely divided carbon black pigment comprising particles having diameters not greater than 25 millimicrons and basic triarylmethane dye in a volatile isoparaffinic hydrocarbon having dissolved therein a dispersing amount of a hydrocarbon-soluble acrylic copolymer resin and also about 0.01 to 3 parts of a polyvalent metal soap and thereby forming a dispersion of carbon black agglomerates, said acrylic copolymer resin being a terpolymer of vinyltoluene, a branched-chain butyl methacrylate and lauryl or stearyl methacrylate,

b. and then breaking down a part but not all of said carbon black agglomerates into particles having a size smaller than said agglomerates by subjecting the dispersion thereof to high frequency vibration.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,890,240 Dated June 17, 1975

Inventor(s) David L. Hochberg

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

The term of this patent subsequent to October 17, 1989, has been disclaimed.

Signed and Sealed this

Twentieth Day of July 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks