United States Patent Office 3,542,681 Patented Nov. 24, 1970

3,542,681

NEGATIVE WORKING ELECTROSTATIC TONERS

Thomas D. Mutaffis, North Plainfield, N.J., assignor to GAF Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed July 10, 1968, Ser. No. 743,592
Int. Cl. G03g 9/04
U.S. Cl. 252—62.1 9 Claims

ABSTRACT OF THE DISCLOSURE

A negative-working electrostatic toner composition capable of providing a reverse black and white image in an electrostatic reproduction process comprising an electrically insulating carrier liquid, a pigment or coloring agent, e.g. carbon black, and a polymeric material capable of imparting the negative-working characteristics to the electrostatic toner composition. Such a polymeric material preferably comprises an alkylated polymer of a heterocyclic N-vinyl monomer.

The present invention relates to a liquid toner composition for use in electrostatic printing processes; more particularly, the present invention relates to a negative-working liquid toner system comprising in addition to an electrically conductive carrier liquid, a pigment or coloring agent, and a polymer which contributes the negative-working characteristics to the toner composition.

In an electrostatic reproduction process a liquid toner is generally employed. In such electrostatic processes in which a liquid toner is employed, a first latent electrostatic image is produced generally on a photoconductive surface, e.g. zinc oxide, by a first application of an overall negative charge. This is followed by a discharging through light exposure so as to leave a negative charge in the unexposed areas. It is at this point that the liquid toner composition is applied. In case of positive-working toners, the particles of the toner composition comprising the pigment or coloring agent are positively charged, and accordingly, are directed to the negatively charged areas of the latent image. In the case of the electrostatic reproduction process briefly described above, this results in the production generally of a black on white reproduction through the utilization of positively charged pigments, e.g. carbon black.

In the case of negative-working toners, however, the particles of toner, e.g. carbon black or similar pigment or coloring agent, are negatively charged and as such, are repelled by the latent electrostatic image and attracted by the background areas. Using a pigment such as carbon black, therefore, this results in a reverse image from the original and provides for the production for a white on black print.

In most instances, when a pigment such as carbon black is suspended in an insulating liquid, it assumes mixed low, polarities. As proposed in various patents the positive polarity of the toner particles can be easily intensified by the addition of various control agents to a dispersion or suspension of the pigments or coloring agents within the insulated carrier of the toner composition.

A different problem, however, results when it is desirable for particular purposes to provide a negative-working liquid electrostatic toner composition which is capable of providing a reverse image, or more particularly, a white on black image in an electrostatic reproduction process. Under such circumstances, it is necessary to provide a liquid toner composition which because of the components thereof, is capable of being attracted to the background area of the latent electrostatic image while being repelled by the latent electrostatic image itself. Accordingly, in order to prepare such a negative-working electrostatic liquid toner system, it is necessary to incorporate within the basic toner comprising the electrically conductive fluid and pigment or coloring agent toner particles a material which when incorporated in such system, acts to induce strong negative polarity on the pigment particles so as to be applicably employed in the production of the negative or reverse image.

As is well appreciated, the development of suitable materials which can convert positive-working toner particles into negative-working particles is much more difficult than merely accentuating the positive characteristics of the toner. Therefore, because of the difficulty in developing a negative-working toner system giving a full, clear negative reproduction print, such toner systems, although extremely desirable for particular purposes, have not been used to great extent. In this respect, as pointed out above, one serious problem of the production of negative-working toners is the development of a composition or system which will yield a clear and full reproduction print, that is, one having no tendency to streak and containing no bleached out areas.

The above deficiencies and disadvantages of prior art negative-working liquid toner compositions for electrostatic printing processes have been overcome in accordance with the present invention through the development of a negative-working liquid toner system which comprises an electrically insulating carrier liquid containing a pigment or coloring agent and a polymeric material capable of providing the negative-working characteristics for the liquid toner composition.

Accordingly, it is a principal object of the present invention to provide such a negative-working liquid toner system for use in electrostatic printing processes which negative-working liquid toner eliminates the inherent deficiencies and disadvantages of the prior art.

A further object of the present invention is to comprise such a negative-working liquid toner system comprising an electrically insulating carrier liquid, a pigment or a coloring agent, and a polymeric material capable of imparting the negative-working characteristics to the liquid toner composition.

A still further object of the present invention comprises such a negative-working liquid toner composition for use in electrostatic printing processes comprising an electrically insulating carrier liquid, a pigment, e.g. carbon black, and a polymeric material capable of imparting the negative-working characteristics to the liquid toner composition, said polymeric material preferably comprising an alkylated polymer of a heterocyclic N-vinyl monomer.

Still further objects and advantages of the novel negative-working liquid toner composition of the present invention will become more apparent from the following more detailed description thereof.

The above objects and advantages of the present invention are provided by a liquid negative-working electrostatic toner comprising an electrically insulating carrier liquid containing a pigment or coloring agent, e.g. carbon black, and a polymeric material capable of imparting the negative-working characteristics to the toner composition, such polymeric material preferably comprising an alkylated polymer of a heterocyclic N-vinyl monomer.

Thus, in accordance with the present invention, the liquid toner composition or system comprises as a base fluid any of the conventional electrically insulating carrier liquids generally employed in liquid developer and toner compositions. Such electrically insulating carrier liquids generally comprise hydrocarbon solvent materials having the necessary di-electric constant, e.g. less than 3 and volume resistivity, e.g. in excess of 10^{10} ohm centimeter so as to be acceptably employed in the electrostatic reproduction process. Thus, for example, the solvent can

comprise various hydrocarbon solvents, e.g. toluene, kerosene and mixtures thereof as well as various commercial petroleum and hydrocarbon solvents, e.g. Isopar having a boiling range of from 300–36° C., or Solveso 100 having a boiling range of from 160–174° C., Shell X4 having a boiling range of from 58–70° C., or Shell X55 having a boiling range of from 58–140° C., can be effectively employed as the electrically insulating carrier liquid of the liquid toner system.

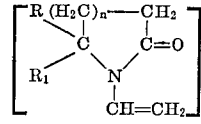
The pigment or coloring agent employed in accordance with the negative-working liquid electrostatic toner composition of the present invention can comprise any of those conventionally employed in positive or negative-working electrostatic toners. In this respect, the negative-working characteristics of the toner are associated with the particular polymeric materials that are included within the liquid system and thus, any conventional pigment or coloring agent can be advantageously employed. Thus for example, the coloring agent or pigment can comprise carbon black and various analogous forms thereof, e.g. channel black, furnace black, lamp black and other black materials made by processes well known in the art, colored pigments including the phosphotungstates and phosphomolybdate colors, alkali blue, and many azo pigments as well as nigrosine dyestuffs and triphenyl methane dyes in particular. Again, these materials are those which are conventionally employed in positive-working and negative-working electrostatic toner compositions. For purposes of the present invention, however, it is preferable to employ one of the afore-mentioned carbon black materials which provide an excellent black background in the electrostatic print produced by employing the liquid toner composition of the present invention.

The pigment or coloring agent, e.g. carbon black when suspended in the carrier liquid as the toner is employed in that amount necessary when attracted to the background of the negative electrostatic image through the negative-working characteristics of the polymeric material which also acts as a dispersing agent because of the surface active characteristics thereof to be deposited on the background areas and provide desired negative print or copy. Generally, the pigment comprises from about 0.01% to about 10% of the toner system or composition. Of course, slightly lesser or greater amounts can be employed when desired for particular purposes.

As indicated above, the negative-working characteristics of the liquid toner composition of the present invention are achieved through the use of certain polymeric materials which are capable of providing the necessary negative-working characteristics. As noted previously, such polymeric materials preferably comprise alkylated polymers of heterocyclic N-vinyl monomer.

These materials are those prepared by alkylation of a homopolymer or copolymer of a heterocyclic N-vinyl monomer, preferably a N-vinyl lactam monomer and most preferably a N-vinyl pyrrolidone monomer with an alpha-olefin containing from 2 carbon atoms to 2000 carbon atoms, preferably in the range of from 2 to 200 carbon atoms, and most preferably in the range of from 8 to 42 carbon atoms, said alkylation process being more fully described in General Aniline & Film Corporation's co-pending patent application, Ser. No. 508,547, filed Nov. 18, 1965 and now U.S. Pat. No. 3,417,054, or by simultaneously polymerizing and alkylating a mixture containing a heterocyclic N-vinyl monomer, a monoethylenically unsaturated polymerizable monomer and an alpha-olefin containing from 2 carbon atoms to 2000 carbon atoms or a mixture of the same or two different heterocyclic N-vinyl monomers and an alpha-olefin containing from 2 carbon atoms to 2000 carbon atoms, said simultaneous polymerization and alkylation process being more fully described in General Aniline & Film Corporation's co-pending patent application, Ser. No. 525,374, filed Feb. 7, 1966 and now U.S. Pat. No. 3,423,367.

As examples of heterocyclic N-vinyl monomers which contain a carbonyl function adjacent to the nitrogen in the heterocyclic moiety, whose alkylated polymer derivatives produced as described in said applications, Ser. Nos. 508,547 and 525,374, may be employed in practicing the present invention, that may be mentioned are N-vinyl succinimide, N-vinyl diglycolylimide, N-vinyl glutarimide, N-vinyl-3-morpholinone, N-vinyl-5-methyl-3- morpholinone, N-vinyl-5-methyl-3-morpholinone, N-vinyl-5-ethyl-3-morpholinone, N-vinyl oxazolidone, etc., and N-vinyl ringoxygenated lactams as disclosed in U.S. Pat. 3,231,548, and especially the N-vinyl 5-, 6- and 7-membered lactams, particularly N-vinyl pyrrolidone, characterized by the following formula:



wherein R and R_1 are selected from the group consisting of hydrogen, methyl and ethyl, n is an integer of from 1 to 3, and m represents the average molecular weight as determined by relative viscosity measurements which are designated as K values.

The viscosity coefficient, K, which is fully described in Modern Plastics, vol. 23, No. 3, pp. 157–61, 212, 214, 216 and 218 (1945) is calculated as follows:

$$\frac{\log \eta_{rel}}{c} = \frac{75K_0^2}{1-1.5K_{0c}} + K_0 \text{ and } K = 1000\,K_0$$

where c is the concentration in grams per 100 ml. of polymer in solution and the η_{rel} is the viscosity of the solution compared to solvent.

There may also be used the alkylated polymers of comparable monomers of N-vinyl 5-, 6- and 7-membered thiolactams, N-acryloylpyrrolidone, -piperidone and -caprolactam; N-acryloyl-5-methyl-pyrrolidone, N-acryloyl-6-methyl piperidine and N-acryloyl-7-methyl caprolactam and their corresponding 5-, 6- and 7-ethyl derivatives; N-acyloxy-methyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxy-ethyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxy-methyl-5-methyl pyrrolidone, -6-methyl-piperidone and -7-methyl-caprolactam; N-methacrylamido-methyl-, N-methacrylamidoethyl-, N-methacrylamidopropyl- and N-(N-phenylacrylamidopropyl)-pyrrolidones, -piperidones and caprolactams.

The homopolymers of the N-vinyl lactams characterized by the foregoing formula (whose alkylated derivatives obtained, for example, as described in said application Ser. No. 508,547, are suitable for use in practicing the present invention) are readily obtained by homopolymerizing N-vinyl pyrrolidone; N-vinyl-5-methyl pyrrolidone; N-vinyl-5-ethyl pyrrolidone; N-vinyl-5,5-dimethyl pyrrolidone; N-vinyl-5,5-diethyl pyrrolidone and N-vinyl-5-methyl-5-ethyl pyrrolidone; N-vinyl piperidone; N-vinyl-methyl piperidone; N-vinyl-6-ethyl piperidone; N-vinyl-6,6-dimethyl piperidone; N-vinyl-6,6-diethyl piperidone and N-vinyl-6-methyl-6-ethyl piperidone; N-vinyl caprolactam, N-vinyl-7-methyl caprolactam; N-vinyl-7,7-dimethyl caprolactam; N-vinyl-7-ethyl caprolactom; N-vinyl-7,7-diethyl caprolactam and N-vinyl-7-methyl-7-ethyl caprolactam.

For the purpose of the present invention I employ alkylated derivatives of homopolymers of heterocyclic N-vinyl monomers having a K value from about 10 to 140, preferably from about 30 to 100. These homopolymers are readily obtained by conventional homopolymerization procedures of the foregoing heterocyclic N-vinyl monomers described in U.S. Pats. 2,265,450; 2,317,804; 2,335,454 and many other too numerous to mention in which working examples are given.

Copolymers obtained by copolymerizing 5 to 99 mole percent of the foregoing heterocyclic N-vinyl monomers with 1 to 95 mole percent of a monoethylenically un-

saturated polymerizable monomer and having a K value from about 10 to 140 are readily alkylated in accordance with the present invention to yield products having solubility characteristics dictated by the end use.

The various monoethylenically unsaturated polymerizable monomers, which are copolymerized with any one of the aforementioned heterocyclic N-vinyl monomers in the conventional manner and which will yield copolymers that are readily alkylated in accordance with said application, Ser. No. 508,547, to produce alkylated copolymers alkylated copolymers suitable for use in practicing the present invention, include vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl lactate, vinyl caproate, vinyl caprylate, vinyl oleate and vinyl stearate; acrylonitrile; vinyl ketones; vinyl cyclohexane; styrene; 2-vinyl pyridine, 4-vinyl pyridine; acrylic acid, acrylate ester monomers of the formula:

$$CH_2{=}CHCOOR_2$$

wherein R_2 represents either a straight or branched alkyl of from 1 to 18 carbon atoms or an alkoxyalkyl in which the total number of carbon atoms in the alkyl groups range from 3 to 6.

As examples of such acrylate esters the following are illustrative: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-ethyl-1-butyl, amyl, 3-pentyl, 2-methyl-1-pentyl, 4-methyl-2-pentyl, hexyl, 2-ethyl-hexyl, heptyl, 2-heptyl, octyl, 2-octyl, nonyl, 5-ethyl-2-nonyl, decyl, 2-methyl-7-ethyl-4-undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, 2-methoxyethyl, 2-ethoxyethyl and 2-butoxyethyl acrylate; methacrylic monomers such as methacrylic acid, methyl methacrylate, cyclohexyl methacrylate, isobutyl methacrylate, isoamyl methacrylate, β-methoxy ethyl methacrylate and α-(o-chlorophenyl) ethyl methacrylate, β-phenoxy ethyl methacrylate, α-phenyl ethyl methacrylate, phenyl methacrylate, o-cresol methacrylate, p-cyclohexylphenyl methacrylate, 2-nitro-2-methyl propyl methacrylate, diethylaminoethylmethacrylate, ethylidene acetate methacrylate and glycidyl methacrylate, including esters of halo acrylic acids, such as methyl-2-chloro-acrylate, ethyl-α-chloro-acrylate, phenyl-α-chloro-acrylate, α-ethylacrylic acid; methacrylonitrile; N-alkyl and N-aryl substituted acrylamides such as N-methyl acrylamide, N-ethyl acrylamide, N-propyl acrylamide, N-n-butyl acrylamide, N-n-dodecyl acrylamide, N-n-octadecyl acrylamide, N-N-dimethyl acrylamide, N,N-diethyl acrylamide, N-N-di-n-butyl acrylamide, N-N-di-isobutyl acrylamide, N-cyclohexyl acrylamide, N-N-dicyclohexyl acrylamide, N-phenyl acrylamide, N-p-nitro-phenyl acrylamide, N-α-naphthyl acrylamide, N-β-naphthyl acrylamide, N-methyl-N-phenyl acrylamide, N,N-diphenyl acrylamide, N-benzyl acrylamide, N,N-di-benzyl acrylamide; and grafted monomers of the type disclosed in U.S. Pats. 3,029,219; 3,035,009; 2,036,033 and the like.

A mixture consisting of from 5 to 99 mole percent of any one of the foregoing heterocyclic N-vinyl monomers and from 1 to 95 mole percent of a different heterocyclic N-vinyl monomer, such as for example, N-vinyl lactam with either N-vinyl succinimide, N-vinyl-3-morpholinone, and the like, may also be copolymerized and the resulting copolymer alkylated for use in the present invention.

From numerous experiments connected with the present invention, it has been found that the configuration of the foregoing monoethylenically unsaturated monomers, and numerous others, is immaterial since they all copolymerize in the afore-mentioned proportions with the heterocyclic N-vinyl monomers and yield copolymers which are soluble in the organic solvent or mixture thereof and which are readily alkaylated.

With regard to the α-olefins employed for producing the alkylated polymers used in practicing this invention, it is to be noted at the outset that any α-olefins having a molecular weight from about 28 to as high as about 28,000, may be employed as the alkylating agent for the alkylated polymers of the various heterocyclic N-vinyl monomers. As examples of such α-olefins, the following are illustrative; ethylene, propylene, 1-butene, 1-pentene, 2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 2-methyl-1-pentene, 3-ethyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 2-ethyl-1-hexene, 1-decone, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-docosene, 1-tetracosene, 1-pentacosene and polybutenes of molecular weight of 400 to 2500 may be employed.

While linear α-olefins are preferred because of their commercial availability, numerous isomers of α-olefins ranging from 1-pentene to 1-pentacosene as well as polybutenes may also be employed in the alkylation reaction. The only requirement in such case is that the isomer contained in ethylenic unsaturation in the α-position thereof.

Instead of employing any one of the foregoing individual α-olefins, a mixture of commercially available linear α-olefins produced by cracking petroleum wax or by polymerizing lower olefins may also be used as the alkylating agent. Alpha-olefins in the carbon range of from C_6–C_7; C_7–C_9; C_9–C_{11}; C_{11}–C_{15}, and C_{15}–C_{20} are commercially available and may be used. A mixture of α-olefins containing from 65 to 75 percent of α-olefins of from C_{20} to C_{42} carbon atoms having an average molecular weight of 366 is also commercially available and such mixture is employed in the alkylation reaction.

In addition to the preferred employment as the polymeric material of the alkylated polymers of N-vinyl monomers, and in particular, vinyl pyrrolidone monomers, any and all materials capable of imparting the necessary negative-working characteristics to the liquid toner system can be advantageously employed. Thus for example, the materials in accordance with the present invention can comprise natural hydrocarbon polymers, e.g. Gilsonite resins, thermoplastic polymers of unsaturated hydrocarbons derived from petroleum cracking, e.g. Piccopale resins and oil-soluble C-alkyl succinyl derivatives of polyethyleneimine, e.g. penta or tetra-ethylene imine wherein the alkyl group contains 50 or more carbon atoms, e.g. Oronite resins for example, Oronite 1200 as disclosed in U.S. Pats. 3,219,666 and 3,163,603. All of such materials possess surface active characteristics and thus provide the necessary dispersion of the toner particles in the liquid toner system. More importantly, however, all of such materials possess the property of converting the toner system or composition into a negative-working composition effectively employable in electrostatic printing processes for producing reverse or negative reproductions.

Accordingly, the polymeric materials employed in accordance with the present invention to provide the necessary negative-working characteristics to the liquid toner composition are generally those selected from the group consisting of alkylated polymers of N-vinyl monomers, e.g. alkylated polymers of N-vinylpyrrolidone polymers, natural hydrocarbon polymers, e.g. natural bitumen, thermoplastic polymers of unsaturated hydrocarbons from petroleum cracking, and oil-soluble C-alkyl succinyl derivatives of polyethylene imines.

The amount of such material capable of imparting the negative-working characteristics to the liquid toner composition employed for a given amount of pigment or coloring agent is not critical in accordance with the present invention, such material being employed only in that amount necessary to provide the necessary negative-working characteristics while maintaining a stable suspension or dispersion of the toner. Generally, such material is employed in the range of 0.01–2–3 times the weight of the pigment or coloring agent, and preferably within the range of 1 to 100 parts per 100 parts of the pigment employed.

In accordance with the present invention, the manner by which the liquid toner composition is produced is in no way critical and, accordingly, such composition can be prepared by conventional methods well known in the art.

In this respect, it has been found that a 3-roll mill, ball mill, colloid mills, high speed shear mixers, etc., are all applicable in the production of the dispersions employed in the liquid electrostatic toner system of the present invention. Thus for example, it is conventional to produce a concentrate or ink of the toner and material capable of imparting negative-working characteristics to the composition in an insulating carrier liquid, and subsequently adding such concentration or ink to further insulated carrier liquid to provide the liquid toner composition employed in the electrostatic reproduction process.

The present invention wil now be described by reference to the following specific examples. It is to be understood, however, that such examples are presented for purposes of illustration only, and the present invention is in no way to be deemed as limited thereto.

EXAMPLE I

The following materials were mixed on a 3-roll mill to obtain a uniform dispersion as a heavy ink, by passing over the 3-roll mill 8 times:

	Grams
Raven #15 carbon black	2
Ganex 216 [1]	1
Isopar M [2]	3

[1] An olefin-alkylated polyvinylpyrrolidone of an average olefin carbon chain length of 16 carbon atoms and 20% vinylpyrrolidone residue.
[2] An aliphatic petroleum solvent having a boiling range of 300–360° F.

The ink was adjusted to 5% carbon black content with the addition of a further amount of the electrically insulating carrier liquid and, the final toner system was provided by adding 7 cc. of the 5% toner to 1 liter of additional aliphatic petroleum solvent.

The toner composition was then employed in a conventional electrostatic copier to produce a negative electrostatic reproduction. The print produced by the use of the toner composition of the present invention was found to give a clear reproduction of the original having a reverse image, that is, the background areas of the reproduction were black whereas the printed material on the original was white. A copy having good fill and substantially no tendency to streak was obtained.

EXAMPLE II

Example I is repeated except that the material employed to impart the negative-working characteristics to the liquid toner composition is replaced by a substantially equivalent amount of the following materials:

Ganex 220 [1]
Oronite 1200 [2]
Piccopale resin [3]
Gilsonite [4]

[1] An olefin-alkylated polyvinylpyrrolidone of an average olefin carbon chain length of 20 carbon atoms and 20% vinylpyrrolidone residue.
[2] An oil-soluble C-alkyl succinyl derivative of pentaethylene imine having 50 or more carbon atoms in the alkyl chain.
[3] A thermoplastic polymer of an unsaturated hydrocarbon derived from petroleum.
[4] A natural hydrocarbon polymer-natural bitumen.

In all cases, when such materials are employed in lieu of the alkylated polymer of the N-vinyl monomer, substantial equivalent results are obtained and a negative-working electrostatic toner providing full, clear negative prints is obtained.

While the present invention has been described primarily with respect to the foregoing specific examples, it is to be understood that the present invention is in no way to be deemed as limited thereto, but must be construed as broadly as all or any equivalents thereof.

What is claimed is:

1. A negative-working electrostatic liquid toner consisting essentially of
   (a) an electrically insulating carrier liquid having a dielectric constant of less than 3 and a volume resistivity in excess of 10^{10} ohm centimeter;
   (b) a coloring agent dispersible in said carrier liquid and capable of yielding color copies when repelled by a negative latent image; and
   (c) as a polymer capable of imparting negative-working characteristics to said toner, an alkylated polymer of a heterocyclic N-vinyl monomer in which the alkyl radical of said polymer contains from 2 to 2000 carbon atoms and said polymer has a K value of about 10 to 140.

2. A toner as defined in claim 1 wherein said coloring agent is a pigment.

3. A toner as defined in claim 2 wherein said pigment is carbon black.

4. A toner as defined in claim 1 wherein said carrier liquid is a hydrocarbon.

5. A toner as defined in claim 1 wherein said alkyl radical of said polymer contains 8 to 42 carbon atoms.

6. A toner as defined in claim 1 wherein said alkylated polymer is an alkylated polymer of an N-vinylpyrrolidone monomer.

7. A toner as defined in claim 6 wherein said coloring agent is a pigment.

8. A toner as defied in claim 7 wherein said pigment is carbon black.

9. A toner as defined in claim 4 wherein said carrier liquid is a hydrocarbon.

References Cited

UNITED STATES PATENTS

3,079,270	2/1963	Cortez	252—62.1

FOREIGN PATENTS

938,293	1963	Great Britain.
993,150	1965	Great Britain.
944,345	1963	Great Britain.
944,394	1963	Great Britain.

GEORGE F. LESMES, Primary Examiner

J. P. BRAMMER, Assistant Examiner