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CARBON PAPER INKS AND METHOD FOR MAKING SAME

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This invention relates generally to carbon paper inks containing an additive for imparting desired characteristics thereto and the method of preparing carbon paper inks containing this additive.

Carbon paper is the term applied to a paper coated with a waxy material in which sufficient dye or pigment has been incorporated to give color. In the trade, the paper is generally known as the base sheet, its weight being used for purposes of classification. The color producing coating material is known as the carbon paper ink.

The base sheet varies in weight from the very thin tissue, weighing 4 pounds to a ream which contains 500 sheets (20 x 30 inches), to paper which may weigh 16 pounds or more to the ream, depending upon the use to which the carbon paper is to be put.

The amount of carbon paper ink coated on the base sheet depends upon the number of carbon copies required from the carbon paper. A greater number of copies may be expected through the employment of a heavier coating.

The coating generally employs as a base, vegetable, mineral, animal or synthetic waxes such as carnauba, ceresine, beeswax and paraffin. The color may be produced by the use of a pigment or a dye carried in a vehicle such as mineral or vegetable oil. Filler may, if desired, be added to serve as an extender for the dye. The carbon paper ink can be applied by roller or knife coating methods, using a hot melt which is set by passing over chilled rollers.

A good carbon paper should be clean and non-smutting. The coating should be applied evenly and smoothly and there should be no pin holes or other imperfections in the backer sheet. It should lie flat on a smooth surface for ease of handling by the operator.

An important problem in the manufacture of carbon paper, particularly in the manufacture of carbon paper used in autographic registers is the prevention of adherence of the carbon paper to the record sheet or roll. This adherence causes the carbon papers and/or the record sheets to tear when they are separated. The applicant has now discovered that the addition of silicones to the carbon paper ink with which the base sheet is coated, substantially reduces the adhesion of the carbon paper to the record sheet. Because the adhesion increases as the thickness of the coating employed is increased, and because of the applicant's discovery that silicones incorporated into carbon paper inks reduce stick, the thickness of the carbon coating may be increased substantially, thus enhancing the usefulness of the carbon paper. In other words, by reducing tackiness or stick the amount of coating may be increased, thus extending the number of good, legible copies which can be obtained from the carbon paper. This invention has thus produced a notable advance in the art, particularly

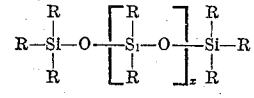
in the manufacture of multiple-use carbon papers. The addition of silicone to carbon paper ink has also found great utility in a vast variety of specialized reproducing apparatus including, for example, autographic registers which require a carbon paper with a minimum of tackiness. The efficiency of such reproducing apparatus is substantially reduced due to the fact that carbon paper tackiness ordinarily increases considerably under conditions of hot weather and high humidity. Under these conditions, operating difficulties in autographic registers, for example, are increased, for the most part, due to the register feeding means tearing the carbon paper and/or the record sheets when the feeding means attempts to release the carbons from the written record sheets. With the addition of silicone to the carbon paper ink this difficulty is significantly diminished and in many cases eliminated.

It is thus the principal object of the present invention to provide carbon paper ink formulations containing silicones, which are vastly superior in their antistick properties to carbon paper ink formulations hitherto known.

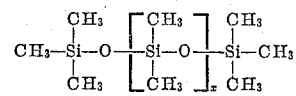
It is a further object of the present invention to provide new and improved ink formulations which can be employed in the manufacture of high-grade, multi-use carbon papers without retooling of the manufacturing equipment.

Another object of the present invention is to provide new and improved ink formulations which can be employed in a comparatively heavy coating on register carbon papers and the like, to extend the writing life of the carbons without increasing undesirable tackiness.

With these and other objects in view, as will become apparent from the following detailed description, this invention contemplates the provision of a silicone additive for carbon paper inks and the like which may be used in varying amounts and widely different viscosities for the purposes indicated. In industrial practice the terms, silane, siloxane, etc., are generally disregarded, and the term silicone has come to be a generic term covering all compounds containing silicon and organic groups in the molecule, provided that the silicon is present in sufficient amount to affect the properties measurably. The group of silicones which are preferred in the present invention are the type,



where R is an alkyl group, an aryl group, or a hydrogen atom and x is the number of recurring monomeric units. These compounds generally comprise the class called silicone fluids and are linear polymers of alternating silicon and oxygen atoms, each silicon atom having two organic groups attached thereto. Dimethyl silicone fluids, or more precisely dimethylpolysiloxanes which have been used with great success have the formula:



where x is the number of recurring monomeric units. The larger the x or the molecular weight, the higher is the viscosity. The fluids are water clear with an oily feel.

By way of example, one silicone of the type employed in this invention is Linde L-45 silicone oil which is

produced by the Linde Air Products Company, and has the following specifications:

Viscosity @ 25° C.	centistokes	350
$D_{25/25}$		0.972
Refractive index @ 25° C.		1.403
Flash point	° F. min.	600
Viscosity temperature Coefficient		0.60

$$1-\frac{V_{210^\circ F.}}{V_{100^\circ F.}}$$

In a carbon paper study, all concentrations of the dimethyl silicone fluids tested from 1% to 10% by weight were completely effective in substantially or completely removing stick. The higher concentrations had no bad effects.

Thus, with coatings up to 8 lbs. (20" x 30"—500 sheets) as little as 1% by weight of a dimethyl fluid substantially or completely eliminated stick. With coatings of 8 to 10 lbs. 5% by weight dimethyl fluid substantially or completely eliminated stick.

A viscosity of 100,000 centistokes at 25° C. may be considered, as a practical matter, the maximum for effective stick removal. Viscosity of 20 centistokes at 25° C., is effective and may be considered the minimum value of viscosity range for practical purposes. It will readily be understood, however, that the viscosity may vary considerably above and below this range without departing from the spirit of the invention or significantly effecting the diminution of stick.

Dimethyl silicone fluids having viscosities in the range of from 20 centistokes to 10,000 centistokes at 25° C. are completely effective in removing stick. This stick removal effect is readily apparent immediately after coating and before aging.

In the case of 100,000 centistokes dimethyl silicone fluid full reduction of stick does not occur immediately upon coating. However, after aging the carbon paper, the 100,000 centistokes fluid is as effective as those having lower viscosity.

Thus, while it is not intended in any way to limit the viscosity of the silicones employed to 100,000 centistokes, the lower viscosities have been found to adequately remove carbon paper stick. Since the employment of silicones with viscosity higher than 100,000 centistokes inherently result in carbon paper manufacturing difficulties as well as otherwise unjustifiable carbon paper aging time these silicones, though effective, are not considered the most desirable.

In carbon paper technology, the stick value or tendency for the carbon paper to adhere to the record sheets upon which the writing takes place is determined by collating the carbon sheet or sheets between two or more of the record sheets and writing on the uppermost record sheet, thereby causing some of the carbon ink coating to transfer from the carbon sheet to the record sheet disposed below. The force necessary to remove the carbon paper from the record sheets is then measured with a spring scale in the direction parallel to the plane of the papers. This measurement is made with numerous replications in a statistically designed experiment, specifically a Latin Square which cancels out the variations in handwriting and wear on the pencil. The average of the values resulting from this testing is considered to be the measure of stick.

In one such stick test showing the effectiveness of silicones having different viscosities, a paste comprising 13.1 lbs. castor oil, 18.6 lbs. 100 S. S. U. ink oil, 2.0 lbs. lecithin, 6.6 lbs. Victoria Pure Blue dye and 40.0 lbs. calcium carbonate was ground on a three-roll mill to a fineness of Production Club #10 on a Hegeman gauge. Carnauba wax, 19.7 lbs., and 5% by weight of dimethyl silicone fluids of six different viscosities were stirred into the paste and the ink formulation coated on an 11 lb. (20" x 30"—500 sheets) base sheet with deposits in the range of 7.0 to 7.6 lbs. (20" x 30"—500). Stick tests were made on this carbon paper with the following results:

Viscosity of Silicone @ 25° C.	Silicone Concentration 5% by Weight of Total Ink Formula	Average Stick Values in 10 Gram Units
	Percent	
No silicone (control)	5	27.1
20 Ctsks. dimethyl silicone fluid	5	0.0
350 Ctsks. demethyl silicone fluid	5	1.0
1,000 Ctsks. dimethyl silicone fluid	5	1.0
5,000 Ctsks. dimethyl silicone fluid	5	0.9
10,000 Ctsks. dimethyl silicone fluid	5	0.0
100,000 Ctsks. dimethyl silicone fluid	5	17.3

The above stick tests were made before the carbon was aged. After aging approximately seven weeks the 100,000 centistokes silicone had produced a stick value of 0.0.

In another stick test showing the effectiveness of silicones having different viscosities, a paste comprising 28 lbs. Milori Blue pigment, 12 lbs. calcium carbonate, 2 lbs. lecithin, and 38 lbs. 100 S. S. U. ink oil was ground on a three-roll mill to a fineness of Production Club #10 on a Hegeman gauge. 20 lbs. of carnauba wax and dimethyl silicone fluids of five different viscosities were stirred into the paste and the ink formulation coated on an 11 lb. (20" x 30"—500 sheets) base sheet with deposits in the range of 7.5 to 8.5 lbs. (20" x 30"—500 sheets). Stick tests were made on this carbon paper with the following results:

Viscosity of Silicone @ 25° C.	Silicone Concentration 1% by Weight of Total Ink Formula	Average Stick Values in 10 Gram Units
	Percent	
No silicone (control)		27.9
20 Ctsks.	1	0.0
350 Ctsks.	1	0.0
1,000 Ctsks.	1	0.0
5,000 Ctsks.	1	0.4
100,000 Ctsks.	1	15.0
20 Ctsks.	10	0.0
350 Ctsks.	10	0.0
1,000 Ctsks.	10	2.2
5,000 Ctsks.	10	5.2
100,000 Ctsks.	10	12.0

After aging for three weeks the addition of 1% of dimethyl silicone fluid of 5,000 ctsks. and 100,000 ctsks., and the addition of 10% of dimethyl silicone fluid of 1000 ctsks., 5000 ctsks. and 100,000 ctsks. showed stick readings of 0.0.

It has been suggested that these highly desirable results are due to the fact that the silicone is incompatible with the carbon paper ink and, consequently, migrates to the surface where it decreases stick. This theory seems to be borne out by the fact that the more insoluble the silicone is in mineral oil, the better its anti-stick properties. Since the higher the viscosity, the lower the solubility of the silicone in mineral oil, the range of silicones which function effectively to decrease stick in carbon paper inks has an extremely broad range. Whatever the theory for the effectiveness of silicones in inhibiting stick when added to carbon paper inks, it is certainly clear that their addition brings about results which are both surprising and of the greatest commercial value, thus constituting a significant advance in ink technology.

For a fuller understanding of the nature of the present invention, reference may be had to the following examples:

Example I

13.1 lbs. castor oil, 18.6 lbs. 100 SSU ink oil, 2.0 lbs. lecithin, 6.6 lbs. Victoria Pure Blue dye, and 40.0 lbs. calcium carbonate were mixed and ground to Production Club No. 10 on a Hegeman gauge in a roller mill. Approximately 19.7 lbs. carnauba wax and 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone

fluid having a viscosity of 20 centistokes at 25° C. was added to the finished ground ink while the ink was stirred at a temperature of approximately 93° C. The ink, while molten, was coated on a carbon tissue. The ink was then solidified by chilling which caused the wax in the vehicle to freeze. 9 lbs. of this ink formula (20" x 30"—500) were deposited on an 11 lb. (20" x 30"—500) backer sheet.

Example II

The same procedure was followed as in Example I with the exception that approximately 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 100,000 centistokes at 25° C. was employed.

Example III

The same procedure was followed as in Example I with the exception that approximately 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was added to the finished ground ink.

Example IV

The same procedure was followed as in Example I with the exception that approximately 2.0 lbs. or 2% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was added to the finished ground ink.

Example V

The same procedure was followed as in the preceding example with the exception that approximately 3.0 lbs. or 3% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was employed.

Example VI

The identical procedure was used as in the preceding examples with the exception that approximately 4.0 lbs. or 4% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was employed.

Example VII

The identical procedure was used as in the preceding examples with the exception that approximately 5.0 lbs. or 5% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 20 centistokes at 25° C. was used.

Example VIII

The identical procedure was used as in the preceding examples with the exception that approximately 5.0 lbs. or 5% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 1000 centistokes at 25° C. was used.

Example IX

The identical procedure was used as in the preceding examples with the exception that approximately 5.0 lbs. or 5% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 5000 centistokes at 25° C. was used.

Example X

The same procedure was followed as in the preceding examples with the exception that approximately 5.0 lbs. or 5% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 100,000 centistokes at 25° C. was employed.

Example XI

The same procedure was followed as in the preceding examples with the exception that approximately 5.0 lbs. or 5% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was used.

Example XII

The same procedure was followed as in the preceding examples with the exception that approximately 7½% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was used.

Example XIII

The identical procedure was used as in the preceding examples with the exception that approximately 10% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 20 centistokes at 25° C. was added to the finished ground ink.

Example XIV

The identical procedure was used as in the preceding example with the exception that approximately 10% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 100,000 centistokes at 25° C. was used.

Example XV

The identical procedure was used as in the preceding examples with the exception that approximately 10% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was employed.

Example XVI

In this example a different ink formula was used comprising 13.1 lbs. castor oil, 13.4 lbs. 100 SSU ink oil, 2.2 lbs. lecithin, 6.6 lbs. Victoria Pure Blue dye, 44.9 lbs. asbestine, and it was mixed and ground to Production Club No. 8½ on a Hegeman gauge in a roller mill. Approximately 19.7 lbs. carnauba wax and 5% of the weight of the total ink formula of dimethyl silicone fluid having a viscosity of 350 centistokes at 25° C. was added to the finished ground ink while the ink was stirred at a temperature of approximately 90° C. The ink, while molten, was coated on a base sheet. The ink was then solidified by chilling which caused the wax in the vehicle to freeze. 12 lbs. (20" x 30"—500) of this ink formula were deposited on an 11 lb. (20" x 30"—500) base sheet.

Example XVII

28.0 lbs. Milori Blue, 12.0 lbs. calcium carbonate, 2.0 lbs. lecithin, 38.0 lbs. 100 SSU ink oil were mixed and ground in a three-roll mill to a fineness of grind of Production Club No. 10 on a Hegeman gauge. The ground paste was then mixed with 20.0 lbs. of carnauba wax and heated to 79° C. A quantity of the ink so prepared was used to produce carbon paper for repetitive stick tests without the benefit of silicones in the carbon paper ink. Approximately 1.0 lbs. or 1% of the total ink formula of dimethyl silicone fluid, having a viscosity of 20 centistokes at 25° C., was added to a portion of the finished ground ink while the ink was stirred at a temperature of 93° C. The ink, while molten, was coated on a carbon tissue. The ink was then solidified by chilling, which caused the wax in the vehicle to freeze. 7.5–8.5 lbs. of this ink formula was deposited on an 11 lb. (20" x 30"—500) base sheet.

Example XVIII

The same procedure was followed as in Example 17, with the exception that approximately 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 350 centistokes at 25° C. was employed.

Example XIX

The same procedure was followed as in Example 17, with the exception that approximately 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 1,000 centistokes at 25° C. was added to the finished ground ink.

Example XX

The same procedure was followed as in Example 17, with the exception that approximately 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 5,000 centistokes at 25° C., was added to the finished ground ink.

Example XXI

The same procedure was followed as in Example 17, with the exception that approximately 1.0 lb. or 1% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 100,000 centistokes at 25° C., was employed.

Example XXII

The same procedure was followed as in Example 17, with the exception that approximately 10.0 lbs. or 10% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 20 centistokes at 25° C., was employed.

Example XXIII

The same procedure was followed as in Example 17, with the exception that approximately 10.0 lbs. or 10% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 350 centistokes at 25° C., was added to the finished ground ink.

Example XXIV

The same procedure was followed as in Example 17, with the exception that approximately 10.0 lbs. or 10% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 1,000 centistokes at 25° C., was used.

Example XXV

The same procedure was followed as in Example 17, with the exception that approximately 10.0 lbs. or 10% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 5,000 centistokes at 25° C., was employed.

Example XXVI

The same procedure was followed as in Example 17, with the exception that approximately 10.0 lbs. or 10% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 100,000 centistokes at 25° C., was added to the finished ground ink.

All of the above formulations gave results in terms of reduction of stick which were comparable to the previously formulated values.

It will be readily understood that the present invention encompasses the incorporation of silicon fluid into carbon paper inks generally and is not limited to the specific formulations set forth by way of example. Thus, the incorporation of silicone into a carbon paper ink of the following general formula will reduce stick:

Ingredient	Proportions
Non-drying oil (such as Castor oil)	15% to 30%.
Interface modifier (such as lecithin)	0% to 5% of solids weight.
Hard wax (such as carnauba)	6% to 25%.
Dye (such as Victoria Pure Blue)	6% to 12%.
Or pigment (such as Milori Blue)	18% to 35%.
Filler or extender (such as calcium carbonate)	0% to 45%.

In other words, the addition of silicones to any carbon paper ink exhibiting stick and generally known to the art will reduce this stick. It will, consequently, be readily appreciated that the present invention is not limited in any way to the specific carbon paper ink formulations set forth by way of example.

Some carbon paper ink formulas employable in the invention do not need an interface modifier or a filler. For example, it has been found that when ouricury wax is employed instead of carnauba the addition of an interface modifier is unnecessary. When a pigment is employed instead of a dye, a filler is frequently not used because the pigment is low enough in cost to justify sufficiently liberal use of it to make the filler unnecessary. It will thus be readily understood that the present invention encompasses the addition of dimethyl polysiloxane into ink formulas which do not contain filler and interface modifier as well as those which do contain these ingredients.

Generally speaking, it has been found the heavier the coating of ink the greater the quantity of silicone necessary. However, variation in the silicone requirement is not believed to be due to the kind and weight of the base sheet tissue or to the fineness of grind employed. In fact, reasonable variations in the fineness of grind and the kind and weight of base sheet employed does not materially alter the effectiveness of the silicone in reducing stick. It has been further observed that ball milling produces more tacky inks than stirring. All in all, however, the method of mixing the silicones into the ink does not appear to be of great significance. Also, whether the coating was spread by knife or roller was found not to be critical.

While the invention has been described in detail with respect to particular ink formulations, it is to be understood that the concept of this invention is not limited to the incorporation of silicones into these specific ink formulations but contemplates the incorporation of silicones, particularly dimethyl silicone fluids or dimethylpolysiloxanes, into carbon paper inks generally.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A carbon paper coating composition consisting essentially of 15–30% of a non-drying liquid oil; 0–5% of an interface modifier; 6–25% of a hard wax; a coloring agent selected from the group consisting of a dye in the amount of 6–12% and a pigment in the amount of 18–35%; 0–45% of a filler; and 1–10% of dimethyl silicone fluid having a viscosity in the range of 20–100,000 centistokes at 25° C.

2. As an article of manufacture, paper coated with the composition of claim 1.

3. A carbon paper coating which effectively reduces carbon paper adhesion to record sheets, which comprises a carbon paper ink formulation having by weight 13.1% castor oil, 18.6% 100 SSU ink oil, 2.0% lecithin, 19.7% carnauba wax, 6.6% Victoria Pure Blue dye, and 40.0% calcium carbonate together with 1% through 10% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

4. A carbon paper coating for effectively reducing carbon paper adhesion to record sheets, which comprises a carbon paper ink formula having by weight 38.0% 100 SSU ink oil, 2.0% lecithin, 20.0% carnauba wax, 28.0% Milori Blue, and 12.0% calcium carbonate together with 1% through 10% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

5. A carbon paper coating which effectively reduces carbon paper adhesion to record sheets, which comprises a carbon paper ink formulation having by weight 13.1% castor oil, 18.6% 100 SSU ink oil, 2.0% lecithin, 19.7% carnauba wax, 6.6% Victoria Pure Blue dye, and 40.0% calcium carbonate together with 5% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

6. A carbon paper coating which effectively reduces carbon paper adhesion to record sheets, which comprises a carbon paper ink formulation having by weight 13.1% castor oil, 13.4% 100 SSU ink oil, 2.2% lecithin, 19.7% carnauba wax, 6.6% Victoria Pure Blue dye, 44.9% asbestine together with 5% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

7. As an article of manufacture, carbon paper comprising paper to which has been applied a coating of carbon paper ink having by weight 13.1% castor oil, 18.6% 100 SSU ink oil, 2.0% lecithin, 19.7% carnauba wax, 6.6% Victoria Pure Blue dye, and 40.0% calcium carbonate and 1% through 10% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

8. As an article of manufacture, carbon paper comprising paper, carbon paper ink having by weight 13.1% castor oil, 13.4% 100 SSU ink oil, 2.2% lecithin, 19.7% carnauba wax, 6.6% Victoria Pure Blue dye, 44.9% asbestine and 1% through 10% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

9. As an article of manufacture, carbon paper comprising paper, carbon paper ink having by weight 38.0% 100 SSU ink oil, 2.0% lecithin, 20.0% carnauba wax, 28.0% Milori Blue, 12.0% calcium carbonate and 1% through 10% of the total weight of said ink of dimethyl silicone fluid having a viscosity ranging between 20 centistokes and 100,000 centistokes at 25° C.

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