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 heat 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 adherence of the carbon paper to the record sheet. Because the adherence 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 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 anti-stick 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, multiple-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, silicone, 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,

\[
R - \text{Si} - \text{O} - \text{Si} - R
\]

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:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

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:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity @ 25°C</td>
<td>250</td>
</tr>
<tr>
<td>Refractive index @ 25°C</td>
<td>1.405</td>
</tr>
<tr>
<td>Flash point</td>
<td>600 F. min.</td>
</tr>
<tr>
<td>Viscosity temperature</td>
<td>0.60</td>
</tr>
</tbody>
</table>

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 affecting the elimination 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 silicone 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 other unattainable carbon paper aging times, 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 colliding 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 until 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:

<table>
<thead>
<tr>
<th>Viscosity of Silicone @ 25°C</th>
<th>Silicone Concentration % by Weight of Total Ink Formula</th>
<th>Average Stick Values in 10 Gram Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>No silicone (control)</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>200 Cts.</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>500 Cts.</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1,000 Cts.</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>5,000 Cts.</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>10,000 Cts.</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>100,000 Cts.</td>
<td>0.0</td>
<td>17.3</td>
</tr>
</tbody>
</table>

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:

<table>
<thead>
<tr>
<th>Viscosity of Silicone @ 25°C</th>
<th>Silicone Concentration % by Weight of Total Ink Formula</th>
<th>Average Stick Values in 10 Gram Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>No silicone (control)</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>200 Cts.</td>
<td>0.0</td>
<td>27.1</td>
</tr>
<tr>
<td>500 Cts.</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1,000 Cts.</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>5,000 Cts.</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>10,000 Cts.</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>100,000 Cts.</td>
<td>0.0</td>
<td>17.3</td>
</tr>
</tbody>
</table>

After aging for three weeks the addition of 1% of dimethyl silicone fluid of 5,000 cts., and 100,000 cts., and the addition of 10% of dimethyl silicone fluid of 1000 cts., 5000 cts. and 100,000 cts. 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 1**

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 were mixed and ground in Production Club #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 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 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 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 10.0 lb. 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 employed.

Example XXII

The same procedure was followed as in Example 17, with the exception that approximately 10.0 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.

Example XXIII

The same procedure was followed as in Example 17, with the exception that approximately 10.0 lb. or 10% of the weight of the total ink formula of dimethyl silicone fluid, having a viscosity of 35 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 lb. 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 lb. 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 lb. 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 silicone fluid into carbon paper ink 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% of solids weight
Interface modifier (such as lecithin)................... 0% to 8% of solids weight
Hard wax (such as carnauba)............................... 0% to 50% of solids weight
Dye (such as Victoria Pure Blue)......................... 0% to 25% of solids weight
Or pigment (such as Milioli Blue)......................... 0% to 40% of solids weight
Filter or extender (such as caustic carbonate)........... 0% to 45% of solids weight
```

In other words, the addition of any one or 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 require an interface modifier or a filler. For example, it has been found that when oricurry 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 a carbon ink formula 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 do 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 inks 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, 6.5% Victoria Pure Blue dye, and 49.0% calcium carbonate together with 1% through 10% of the total weight of said ink 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 formulation having by weight 38.0% 100 SSU ink oil, 2.0% lecithin, 20.0% carnauba wax, 28.0% Milioli 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, 6.5% Victoria Pure Blue dye, 44.9% base mixture, and 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, 6.5% Victoria Pure Blue dye, 44.9% base mixture, and 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% asbestos 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.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Inventor</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,614,490</td>
<td>Poorman</td>
<td>Jan. 18, 1927</td>
</tr>
<tr>
<td>2,139,092</td>
<td>Neidich</td>
<td>Dec. 6, 1938</td>
</tr>
<tr>
<td>2,299,014</td>
<td>Foster</td>
<td>Oct. 13, 1942</td>
</tr>
<tr>
<td>2,527,793</td>
<td>Bump et al.</td>
<td>Oct. 3, 1950</td>
</tr>
<tr>
<td>2,610,921</td>
<td>Ehrlich</td>
<td>Sept. 16, 1952</td>
</tr>
<tr>
<td>2,749,233</td>
<td>Shoemaker</td>
<td>June 5, 1956</td>
</tr>
</tbody>
</table>

OTHER REFERENCES

Patterson: “Silicones for Printing Inks,” American Ink Maker, April 1948 (page 26).