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WRITING MEDIA FOR BALL POINT PEN

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9 Claims. (Cl. 106—22)

The present invention relates generally to writing media and more particularly to non-solid writing media which are particularly advantageous for use in ball point type writing instruments.

During the past few years, considerable time and money has been expended in an effort to produce non-solid writing media for use with ball point pens, which produce a mark which has the appearance of conventional writing "lead" and ink, both black and colored, which flow freely but do not leak from the point, and which do not build up on the ball and produce a dirty point.

It is an object of the present invention, therefore, to provide writing media (both black and colored) for use in ball point type writing instruments, which produce marks which simulate the marks produced by conventional solid "leads" and inks, both black and colored, and which can be made to be penetrating or non-penetrating.

Another object is to provide writing media which flow from the capillary onto the ball point when the latter is rotated, and which return to or are withdrawn into the capillary when rotation of the ball is stopped. More particularly it is an object to provide writing media which have a certain degree of non-wettability relative to the stainless steel ball points and sufficient internal film strength, whereby the writing media remaining on the ball after rotation stops, is retracted from the ball point, back into the capillary space between the ball and its seat.

Yet another object is to provide writing media of the aforementioned type which can be deposited on a writing surface in a line of uniform width and density and which will not spread or smudge.

Briefly, this invention resides in the use of hydroabietyl alcohol with a long chain fatty acid and a colorant such as an aniline dye, graphite, or carbon black, and possibly a natural resin to produce writing media having certain predetermined physical characteristics.

In order for writing media to operate satisfactorily in ball point type writing instruments, i.e. to flow freely and to have sufficient pull-back without leaking from the point so as to provide a clean point when not in use, they must have a certain viscosity and film strength, and possess a certain degree of non-wettability (a function of surface and interfacial tension) relative to a polished stainless steel ball point.

I have discovered that writing media which consist essentially of a hydroabietyl alcohol, a long chain fatty acid such as oleic acid, and a colorant (coloring material and vehicle) meet all of the aforementioned requirements, and operate extremely satisfactorily in a ball point type writing instrument under wide ranges of external physical condition. However, in some instances, the addition of a small quantity of natural resin improves

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the viscosity or body of the media and enhances the "pull-back" characteristics.

The resin, which will be referred to hereinafter as natural rosin, can be either the gum rosin obtained from living trees or the wood rosin as obtained from tree stumps.

Hydroabietyl alcohol is a resinous mono hydric alcohol derived, for example, from rosin, by reduction, or by hydrogenolysis. At room temperatures it is a colorless, viscous, elastomeric liquid.

The hydroabietyl alcohol mixture which I have used is produced by Hercules Powder Co., Inc. of Wilmington, Delaware and designated by it as "Hydrolin A" and/or "Abietol."

It contains approximately 15% dehydroabietyl alcohol, 40% dihydroabietyl alcohol, and 45% tetrahydroabietyl alcohol, and has the following listed physical properties:

Hydroxyl value	5-5.1%.
Percent hydroabietyl alcohol	85-87%.
Saponification number in diethylene glycol	5-14.
Acid number	0.1-4.
Methoxyl value	0.5-1.2.
Unsaturation—weight percentage:	
By hydrogen absorption	.60-.75.
By bromine number	12-30.
Color (50 mm. tube), Lovibond	.5 Amber.
U.S. rosin standard	7.
Softening point, (Hercules drop method)	33° C.
Specific gravity, at 20°/20° C.	1.007-1.008.
Pounds per gallon	8.34.
Refractive index at 20° C.	1.528.
Flash point (Cleveland Open Cup)	185-195° C.
Flame point (Cleveland Open Cup)	217-220° C.
Metal content—spectroscopic analyses	Each less than 1 p.p.m.

The coloring material which is used may be an aniline dye, or graphite, or carbon black, dependent upon whether one desires to produce a black marking or a colored marking. The carbon black or graphite is dispersed in a suitable non-hygroscopic vehicle such as mineral oil, castor oil, or a long chain fatty acid, and the dye is usually dissolved in a long chain fatty acid such as oleic acid. The long chain fatty acid is also used with the media which contain graphite or carbon black because it affects the wettability of the liquid relative to the stainless steel ball point, and thereby is instrumental in causing the media to "pull-back" from the ball when rotation is stopped, thereby providing a clean point. Thus, when oleic acid is used as a true solvent for the dye, it performs the additional function of affecting the wettability of the writing media relative to the ball point.

A typical dye-type coloring material for producing a "black" writing medium comprises 20 to 22% nigrosine black dissolved in 78 to 80% of a low titre good quality oleic acid. The nigrosine dye is preferably dissolved in the oleic acid when the mixture is heated to about 140° F., and the mixing is accompanied by constant agitation.

After the dye is in solution, it is desirable to filter it through several layers of cotton felt or other conventional filtering media, to remove any solid particles which may be present.

The dye solution is then mixed with the hydroabietyl alcohol, preferably at a temperature of approximately 140° F., to reduce the viscosity of the alcohol and thereby facilitate the mixing. The resultant mixture is again subjected to filtration to remove any possible contaminants.

For a ball point pen of a conventional type, size and

fit of the ball, the percentages of the various ingredients would be in the neighborhood of:

7.0%–8.0%	nigrosine black
28.0%–32.0%	oleic acid
60.0%–65.0%	hydroabietyl alcohol
0.0%–7.0%	natural rosin

However, it is to be understood that some slight variations in percentages may be necessary, dependent upon the particular size of the reservoir, the size of the ball point, and the care used in adjusting the ball point in its race or housing. Thus, if there is to be a loose fit, it is necessary to have a medium of heavier viscosity whereas if the ball is to fit tightly in its seat, a medium of lighter viscosity is required.

The approximate viscosity of the above formulation would normally range from about 3500 to 16,000 cps. as determined by a Brookfield viscosimeter using a No. 4 spindle at 80° F. temperature. The preferred range is from about 6500 to about 12,000 cps.

For relatively large ball points and fittings a typical formulation would be:

6%	nigrosine
27%	oleic acid
67%	hydroabietyl alcohol

Under some conditions the addition of another 3–5% natural rosin to the above formulation improves the viscosity characteristics.

To produce a blue-colored writing medium, any one of a number of basic blue dyes can be dissolved in oleic acid and mixed with hydroabietyl alcohol. Lacquer Oil Blue of Tennessee Eastman Co., Kingsport, Tenn., a division of Eastman Kodak Company, when used in the following proportions, produces a highly satisfactory writing medium:

15%	Eastman Lacquer Oil Blue
25%	oleic acid
61%	hydroabietyl alcohol

Here again, the addition of 3–5% natural rosin to this formulation may be helpful in improving its viscosity index.

"Black" or colored writing media embodying the present invention is formulated with an aniline dye, oleic acid and hydroabietyl alcohol in the following range of percentages:

6.0%–15.0%	aniline dye
24.0%–32.0%	oleic acid
60.0%–67.0%	hydroabietyl alcohol

Inasmuch as the dye is soluble in the oleic acid and the oleic acid and hydroabietyl alcohol are compatible, a true solution is formed.

As pointed out hereinabove, hydroabietyl alcohol can also be used with coloring matter such as graphite and/or carbon black. For best results it is necessary to have a dispersion of the graphite and/or carbon black particles in a light mineral oil which, in addition to providing certain body to the writing media, also improves the lubricating qualities of it so that the ball rotates more freely in its seat.

A typical formulation employing graphite is:

15%	graphite
46%	light mineral oil (SAE 40–90)
2%	oleic acid
32%	hydroabietyl alcohol
(3–5%)	natural rosin may also be added)

When carbon black is used a typical formula is:

12%	carbon black
50%	light mineral oil (SAE 40–90)
6%	oleic acid
32%	hydroabietyl alcohol
(3–5%)	natural rosin may also be added)

Although the problem of true color is not so important when nigrosine, carbon black, or graphite is used as the

coloring material, the fact that hydroabietyl alcohol is a colorless substance is of considerable importance when a blue or red dye is used to produce colored writing media.

Writing media produced according to the teachings of this invention can be rolled onto a writing surface by means of a ball point writing instrument, without spreading or blotting and without skipping or globbing.

Furthermore, the writing media are pulled off of the ball and transferred to the writing surface when the writing instrument is in use, but when the writing instrument is moved off the surface and the ball is no longer rotated, the writing media are retracted into the capillary space between the ball and its seat, leaving a clean point which does not have to be capped before the writing instrument is returned to the user's pocket.

Thus, it is apparent that there has been provided writing media for ball point pens, which fulfill all of the objects and advantages sought therefore.

It is to be understood that the foregoing description has been given only by way of illustration and example, and that changes and alterations in the present disclosure which will be readily apparent to one skilled in the art, are contemplated as within the scope of the present invention which is limited only by the claims which follow.

What is claimed is:

1. A writing fluid for use in ball point type writing units consisting only of an aniline dye, oleic acid, and hydroabietyl alcohol.
2. A writing fluid for use in ball point type writing units consisting only of graphite dispersed in mineral oil, oleic acid, and hydroabietyl alcohol.
3. A writing fluid for use in ball point type writing units consisting only of carbon black dispersed in mineral oil, oleic acid, and hydroabietyl alcohol.
4. A writing fluid for use in ball point type writing units consisting essentially of about 6% to about 15% aniline dye, about 24% to about 32% oleic acid, and about 60% to about 67% hydroabietyl alcohol.
5. A writing fluid for use in ball point type writing units consisting essentially of about 6 parts to about 15 parts aniline dye, about 24 parts to about 32 parts oleic acid, about 60 parts to about 67 parts hydroabietyl alcohol, and about 3 to about 5 parts natural rosin.
6. A writing fluid for use in ball point type writing units consisting essentially of about 15% graphite, about 46% mineral oil, about 2% oleic acid, and about 32% hydroabietyl alcohol.
7. A writing fluid for use in ball point type writing units consisting essentially of about 15 parts graphite, about 46 parts mineral oil, about 2 parts oleic acid, about 32 parts hydroabietyl alcohol, and about 3 parts to about 5 parts natural rosin.
8. A writing fluid for use in ball point type writing units consisting essentially of about 12% carbon black, about 50% mineral oil, about 6% oleic acid, and about 32% hydroabietyl alcohol.
9. A writing fluid for use in ball point type writing units consisting essentially of about 12 parts carbon black, about 50 parts mineral oil, about 6 parts oleic acid, about 32 parts hydroabietyl alcohol, and about 3 parts to about 5 parts natural rosin.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,882,172

April 14, 1959

Ben Scobel

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 3, for "nitgrosine black " read -- nigrosine black --;
line 37, for "25% oleic acid" read -- 24% oleic acid --.

Signed and sealed this 3rd day of November 1959.

(SEAL)

Attest:

KARL H. AXLINE
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