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(71) Applicant: Matsushita Electric Industrial Co., Ltd.
1006, Oaza Kadoma
Kadoma-shi Osaka-fu, 571(JP)

(72) Inventor: Soga, Mamoru
1-22, Saikudani-1-chome
Tennoji-ku Osaka(JP)

(72) Inventor: Yubakami, Keiichi
22-7, Korinishinocho
Neyagawa-shi(JP)

(72) Inventor: Sonoda, Nobuo
16-5, Torigainaka-1-chome
Settsu-shi(JP)

(72) Inventor: Shimotsuma, Wataru
12-8, Yamatedai-5-chome
Ibaraki-shi(JP)

(74) Representative: Connor, Terence Kevin et al,
FITZPATRICKS Kern House 61/62 Lincoln's Inn Fields
London WC2B 6EX(GB)

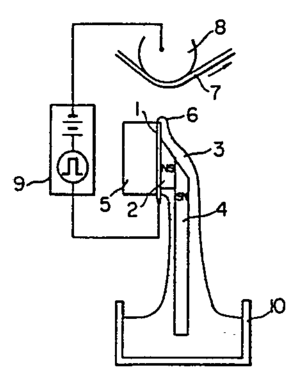
(54) Magnetic fluid.

(57) This invention provides magnetic fluids having various hues.

The magnetic fluids of this invention are constituted of a dispersion of colloidal coloring pigment particles and a dispersion of ferromagnetic particles. Said coloring pigment particles consist of an inorganic pigment such as cobalt blue, carbon black or the like or an organic pigment such as copper phthalocyanine, pigment scarlet or the like, and are dispersed as colloidal particles. By the selection of the coloring pigment particle, a magnetic fluid having a black hue or an arbitrary hue can be obtained.

The magnetic fluids of this invention exhibit their excellent characteristic properties particularly when used as a recording material. For example, when the magnetic fluid of this invention is used as an ink for making a record on high quality paper, no color separation takes place on the paper surface between the magnetic particles and the coloring pigment particles, and the recorded image keeps its hue stably for a long period of time without color change.

FIG. 1



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MAGNETIC FLUID

BACKGROUND OF THE INVENTION

This invention relates to an improvement of magnetic fluid. Concretely, it relates to an improvement of the hue of magnetic fluid.

Usual magnetic fluid is a liquid in which magnetic fine particles of magnetite or the like having a particle size of 50-200 Å are suspended in a dispersion medium by the aid of surfactant. It has a black-brown color, and it keeps stable for a long period of time so that neither sedimentation nor aggregation readily takes place in it. As dispersion medium for such magnetic fluid, paraffin oil, ester oil, silicone oil, water and the like are used. As the surfactant, carboxylic acids such as oleic acid, linoleic acid and the like, as well as cationic surfactants and nonionic surfactants, are used.

Magnetic fluid finds use in extensive fields such as sealing agent, lubricant, sink and float separation, oil-water separating agent, recording material and the like.

The magnetic fluid of this invention can be used in all the above-mentioned fields, and its excellent characteristic properties can be exhibited particularly in the field of recording material.

As the recording process using a magnetic fluid, there have hitherto been proposed the ink jet process utilizing magnetic deviation and the recording process utilizing the protruded part of magnetic fluid by magnetic force (Japanese Patent Kokai (Laid-Open) No. 23,534/79).

As the ink for such recording processes, a magnetic fluid diluted with a dispersion medium to an appropriate viscosity or its mixture with a dye has hitherto been used. The color of this ink is dependent upon the dispersed fine magnetic particles. When the fine magnetic particle is γ-ferrite, magnetite, Mn ferrite, Ba ferrite, Fe-Zn ferrite or Mn-Zn ferrite, it apparently has a black or black-brown color, but it turns to light brown when it is attached on a support such as paper or the like. This tendency becomes stronger as the magnetic particles become finer Y.

Further, when a magnetic fluid is used as a recording material, the recorded image changes its color with time. For example, an ink in which a magnetite dispersion type of magnetic fluid is used is a liquid having a black-brown color. However, if its image is formed on a white high quality paper, the color of the image turns from black-brown to light brown in several weeks. The color change is due to that the dispersed magnetic fine particles are oxidized by air oxygen to form iron oxide (Fe_2O_3). Though inks using other magnetic fine particles show no great color change, their black-brown color is inclined to light brown from the beginning.

As above, it is an important fault of magnetic fluid when used as an ink that the recorded image assumes a light brownish color on support or turns to light brown or yellowish brown with time and that primary colors such as cyan, magenta, yellow, etc. cannot be obtained therefrom.

The color of magnetic fluid can be converted from brown to black by adding a dye as a colorant to the magnetic fluid. However, if a magnetic fluid containing a dye is formed into an image on white high quality paper, the color of image has a more intense light brown hue than the color of magnetic fluid itself. This is due to the difference in permeability into paper between magnetic fine particles and dye molecule. While the magnetic particle has a size of 50-200 Å, the dye molecule has a size of about several ten Å or less so that the latter has a greater permeability into high quality paper and the dye molecule reaches the backside of paper by permeation. Thus, there arises a great difference between the color of magnetic fluid and that of image, which is an important fault of dye-containing magnetic fluid used as an ink.

SUMMARY OF THE INVENTION

The object of this invention consists in providing magnetic fluid having various hue. Particularly it consists in providing a magnetic fluid which, when used as a recording material on a high quality paper is free from color separation between magnetic particle and coloring pigment particle and can give a black-colored image or an arbitrary single color image.

The magnetic fluid of this invention can be obtained by stably dispersing coloring pigment particles in a liquid prepared by dispersing magnetic particles by the aid of surfactant.

BRIEF EXPLANATION OF THE DRAWINGS

Figure 1 is an outlined constructional view of magnetofluidographic apparatus, and Figure 2 is a partial plan view of said apparatus, wherein:

1 is multi-stylus, 2 is magnet for protrusion, 2' is shield plate for the magnet for protrusion, 3 is magnetic fluid, 4 is feeding magnet, 5 is base pedestal, 6 is protrusion, 7 is recording material, 8 is controlling electrode, 9 is voltage applying means and 10 is magnetic fluid tank.

DETAILED EXPLANATION OF THE INVENTION

The magnetic fluid of this invention is characterized by being constituted of magnetic particles stably dispersed by the aid of surfactant and colloidal coloring pigment particles.

In general, typical colloidal particles have a size of about 10 Å to several 1000 Å. The size of colloical coloring pigment particle to be dispersed in this magnetic fluid is 50-1,000 Å. More preferably, the colloidal coloring pigment particle has a size comparable to that of the stably dispersed magnetic particle, namely, 50-200 Å, from the viewpoint of dispersion stability and permeability into paper.

Usually, a pigment exhibits the maximum hiding power when its size is 0.2-0.3 μ, and pigments usually available commercially have this order of size. Howe-ever, since the pigment to be dispersed in the magnetic fluid of this invention should most preferably have a size comparable to that of the magnetic particle in the magnetic fluid, it is necessary to make the usually available pigment more finely divided. As the method for dispersing a pigment into a dispersion medium, it is recommendable to pulverize a mixture of pigment, dispersing medium and dispersion stabilizer for a long period of time by means of ball mill, attritor, sand grinder or the like. Though any of inorganic pigments and organic pigments can be used as the pigment, organic pigments are more preferable than the other in point of coloring power and easiness of pulverization and dispersion. Since inorganic pigments have higher specific gravity and hardness than organic pigments, it takes a longer period of time to pulverize and disperse inorganic pigments than to do organic pigments. Therefore, in the case of inorganic pigments, it is allowable to add a dispersion stabilizer in synthesizing the pigment by wet process before the pigment particle grows up to form a large particle, by which a pigment having a small particle size can be produced. As above, many of the inorganic pigments have a structure similar to that of magnetic particle such as ferrite, which can be dispersed into a form of colloid by a process similar to the wet process for the production of magnetic fluid. As the dispersion stabilizer, surfactants exhibit excellent dispersion stability. Surfactants include anionic surfactants, cationic surfactants, nonionic surfactants, etc., any of which exhibit a dispersing action. However, the action greatly varies with its combination with pigment and dispersion medium. Therefore, surfactants having a functional group readily adsorbable on the pigment are more preferable. For example, when an inorganic pigment consisting of a metallic oxide such as Cobalt Blue is to be dispersed into a hydrocarbon solvent, the dispersion can be successfully achieved by using a long chain aliphatic carboxylic acid giving a carboxylic acid ion having a strong affinity to metallic oxide, such as oleic acid, or its salt.

As the dispersion medium, water or nonaqueous dispersion media can be used. Examples of the non-aqueous dispersion media include hydrocarbon compounds such as paraffins, aromatic compounds, alicyclic compounds and the like; ethers and esters of aromatic and aliphatic compounds; monohydric and polyhydric alcohol compounds; silicone compounds such as decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, octadecamethylcyclononasiloxane and the like; and so on. When the magnetic fluid of this invention is used as an ink, these dispersion media preferably have as low a volatility as possible. Therefore, compounds having a boiling point not lower than 100°C are suitable for use as a solvent for the magnetic fluid.

As ferromagnetic particles, Co, Ni, Fe, their alloys and ferrite compounds can be thought of, among which ferrite compounds are more preferable from the viewpoint of dispersion stability in the presence of surfactant. As ferrite compounds, γ-ferrite, as well as simple divalent ferrites ($M^{2+}Fe^{3+}{}_2O_4$; M is metal atom) such as Mn ferrite, magnetite, Co ferrite, Ni ferrite and the like, can be referred to. Further, as multi-component ferrites, Ni-Zn ferrite, Fe-Zn ferrite, Mn-Zn ferrite, Mn-Fe ferrite, Fe-Ni ferrite and the like can also be referred to. Among them, the multi-component ferrites are resistant to oxidation in the air, and the oxidation hardly progresses particularly in case of Mn-Zn and Ni-Zn ferrites. Further, in a recording process in which as high a magnetization as possible in low magnetic field is required (for example, magnetofluidography, Japanese Patent Kokai (Laid-Open) No. 23,534/79), Mn-Zn ferrite is suitable.

As inorganic pigments, a variety of ones can be utilized. For example, as blue-colored pigments, cobalt blue, ultramarine, Prussian blue, cerulean blue, manganese blue, tungsten blue, molybednum blue and the like can be referred to. As red-colored pigments, red oxide, red lead oxide, molybdenum red, cobalt red and the like can be referred to. As black-colored pigments, carbon black can be referred to as a typical one. Apart from above, pigments of various colors can be used in accordance with the color of magnetic fluid.

In order to make the color of magnetic fluid black and to keep the black color of the printed product prepared by recording an image on a high quality paper or the like with the ink for a long period of time, it is recommendable to disperse a blue-colored pigment in a magnetic fluid dispersion. By it, the brownishly colored magnetic particles formed by the oxidation of magnetic fluid, if it occurs, can be made achromatic by the action of the blue-colored pigment. In order to enhance the blackness of magnetic fluid, it is recommendable to disperse carbon black into it, in addition to the blue-colored pigment.

As the organic pigment usable in this invention, the followings can be referred to. Thus, as examples of blue-colored pigment, there can be referred to phthalocyanine pigments having a high coloring power such as copper phthalocyanine, copper chloride phthalocyanine, metal-free phthalocyanine, sulfonated copper phthalocyanine and the like; as well as Erioglaucine (Peacock Blue Lakes), Gracia Peacock

Blue (Faste Colors), Rhoduline Peacock Blue, Victoria Blue, Methyl Violet (tungstic acid), Methyl Violet (molybdic acid), Methyl Violet (tannic acid lakes) and the like. As examples of red-colored pigment, there can be referred to Para Red, Lithol Rubine, Permanent Red 2B, Pigment Scarlet, Lake Red C, Scarlet Lake 2R, Rose Toner (Fanal Color), Pigment Rubine G (barium, strontium and calcium lakes), Pigment Rubine 3G (barium, strontium and calcium lakes), Alizarine Lake, Lithol Red (sodium salt, barium salt and calcium salt), Toluidine Toner and the like. Among them, the pigments of phthalocyanine type particularly have a very high coloring power and are excellent in light resistance, chemical resistance and heat resistance, so that they are most preferable as the coloring pigment used in this invention. It is needless to say that the above-mentioned pigments are nothing other than some examples for the explanation of this invention, and they do not limit the invention.

Next, examples of this invention will be mentioned below.

In the examples, the recording of image by the use of magnetic fluid was carried out according to magnetofluidography. The outline of the magnetofluidography is as shown in Figure 1.

That is, multistylus 1 is set on base pedestal 5, and magnet for protrusion 2 is attached by bonding to the multistylus 1 in order to magnetize the latter. The magnet 2 for protrusion is equipped with a feeding magnet 4, by which magnetic fluid is sucked up from the magnetic fluid tank 10 and magnetic fluid 3 is fed to magnet for protrusion 2 and multistylus 1. Thus, a protruded port 6 of magnetic fluid 3 having the form shown in Figure 2 is formed on multistylus 1. When a voltage is applied between multistylus 1 and controlling electrode 8 by means of voltage-applying means 9, a Coulomb force is exercised on the tip of protruded port 6. Thus, magnetic fluid 3 flies toward recording material 7 and produces image on recording material 7.

Example 1

A mixture consisting of 100 g of copper phthalocyanine, 50 cc of oleic acid and 750 cc of kerosene was pulverized and dispersed by means of sand grinder (1,600 rpm) for a time period of 7 days. The resulting dispersion was mixed with a paraffin base Mn-Zn ferrite dispersion so that the ratio of copper phthalocyanine to ferrite particle came to 1:10 by weight, and viscosity of the dispersion was adjusted to about 6 cp at 20°C with paraffin. With this dispersion, recording was carried out by magnetofluidography (construction of the apparatus was as shown in Figure 1). The color of magnetic fluid was blue-black, and the color of the printed image was also blue-black. Neither blurring nor separation of color was observable on the high quality paper. Hue of the printed image hardly changed during a period of several months.

Here, viscosity of the magnetic fluid was adjusted to 6 cp at 20^{o}C for the reason that, in magnetofluidography, a lower viscosity of magnetic fluid gives a more ready response of magnetic fluid to electric signal and a clearer image. If the viscosity exceeds 20 cp (20^{o}C), the response of magnetic fluid to electric signal becomes difficult to occur and a clear image is unobtainable. Since a paraffin base magnetic fluid having a viscosity of 6 cp at 20^{o}C keeps a viscosity of about 10 cp at 0^{o}C, the present recording experiment was carried out by using a magnetic fluid of which viscosity had been adjusted to 6 cp at 20^{o}C.

When a magnetic fluid is used for magnetofluidography, a higher magnetization of magnetic fluid at low magnetic field (100 Oe) is more desirable. A magnetization of at least 35 Gauss (100 Oe) is necessary. When the magnetization is lower than 35 Gauss (100 Oe), no clear image is obtainable. This is for the reason that in magnetofluidography a magnetic field of about 100 Oe is applied to the tip of stylus with which protruded part of magnetic fluid is produced and the magnetic fluid is flung in response to recording signal by the Coulomb force, as shown in Figure 1. If printing is carried out continuously, the magnetic fluid at the tip of stylus is consumed.

However, the same amount of magnetic fluid as its consumption is fed from the magnetic fluid tank automatically by the magnetic force of rubber magnet. If magnetization of magnetic fluid is low at this time, the supply of magnetic fluid cannot follow its consumption, so that a deficiency of magnetic fluid takes place at the tip of stylus. As the result, thinning of printed image, or the like, occurs to cause a drop in the quality of printed image.

Example 2

A mixture consisting of 100 g of cobalt blut (NF-250-P, manufactured by Nippon Ferro K.K.), 50 cc of oleic acid and 750 cc of paraffin was pulverized and dispersed for 7 days by means of sand grinder (1,600 rpm). The resulting dispersion was mxied with a paraffin base Mn-Zn ferrite dispersion so that the ratio of cobalt blue to ferrite particles came to 1:4 by weight. After adjusting viscosity of the dispersion to about 6 cp at 20°C by the use of paraffin, a recording experiment was carried out by magnetofluidography. The color of the magnetic fluid was slightly bluish black, and the color of printed image was also nearly the same as it. Neither blurring nor separation of color was observable on high quality paper. The printed image sample scarcely showed a change in hue during several months.

Example 3

A mixture consisting of 100 g of Prussian blue, 50 cc of oleic acid and 700 cc of paraffin was pulverized and dispersed for 10 days by means of sand grinder (1,600 rpm). The resulting dispersion was mixed with a paraffin base Mn-Zn ferrite dispersion so that the ratio of Prussian blue to ferrite particles came to 1:5 by weight. After adjusting viscosity of the dispersion to about 6 cp at 20^{O}C by the use of paraffin, a recording experiment was carried out by magnetofluidography. The color of the magnetic fluid was blue-black, and the printed image also had the same blue-black color. Neither blurring nor separation of color was observable on high quality paper. This sample of printed image scarcely showed a change of hue during several months.

Example 4

The experiment of Example 3 was repeated, except that the Prussian blue was replaced with ultra-marine. The printed image had the same blue-black color as that of magnetic fluid. Neither blurring nor separation of color was observable on high quality paper. No change was observable in hue during several months.

Example 5

A mixture consisting of 100 g of carbon black (M5, manufactured by Mitsubishi Kasei K.K.) and 800 cc paraffin was pulverized and dispersed by means of sand grinder (1,600 rpm) for 7 days. The resulting dispersion was mixed with the copper phthalocyanine dispersion obtained in Example 1 and a paraffin base Mn-Zn ferrite dispersion so that the ratio of copper phthalocyanine, carbon black and ferrite particles came to 1:1:10 by weight. After adjusting viscosity of this magnetic fluid to about 6 cp at 20°C by the use of paraffin, the magnetic fluid was recorded on a high quality paper by magnetofluidography. The color of the printed image was black, and the color of the magnetic fluid was also black. Neither blurring nor separation of color was observable on high quality paper. The hue of the printed image scarcely changed during several months.

Additionally saying, it is also possible to obtain magnetic fluids having various colors in the same manner as above by using water or other organic solvents as dispersion medium, although only paraffin was used as dispersion medium in the examples mentioned above.

As has been mentioned in the examples presented above, there can be provided according to this invention a magnetic fluid which, when used as a recording material, enables a high speed recording, shows no separation of color on high quality paper and gives a high quality record having a stable hue.

Although the magnetic fluid of this invention has been developed as a recording ink utilizing the phenomenon of protrusion of magnetic fluid under magnetic force, it is also usable as a recording ink for ink jet, ball point pen and the like.

CLAIMS:

1. A magnetic fluid characterized by comprising ferromagnetic particles dispersed in a dispersion medium by the action of surfactant and colloidal coloring pigment particles dispersed in said dispersion medium.

2. A magnetic fluid according to Claim 1, wherein said colloidal coloring pigment particles have a particle size of 50-1,000 Å.

3. A magnetic fluid according to Claim 2, wherein said colloidal coloring pigment particles are dispersed by the action of a dispersion stabilizer.

4. A magnetic fluid according to Claim 3, wherein said dispersion stabilizer is a surfactant.

5. A magnetic fluid according to any one of Claims 1-4, wherein said ferromagnetic particles are particles of a ferrite compound.

6. A magnetic fluid according to Claim 5, wherein said ferrite compound is a composite ferrite.

7. A magnetic fluid according to Claim 6, wherein said composite ferrite is Mn-Zn ferrite.

8. A magnetic fluid according to any one of Claims 1-4, wherein said ferromagnetic particles consist of Fe, Co, Ni or their alloy.

9. A magnetic fluid according to any one of Claims 1-8, wherein said dispersion medium is water or an organic solvent.

10. A magnetic fluid according to Claim 9, wherein said organic solvent consists of at least one

member selected from the group consisting of hydrocarbon compounds, ester compounds, ketone compounds, ether compounds, alcohol compounds and silicone compounds.

11. A magnetic fluid according to Claim 1, wherein said coloring pigment consists of at least one member selected from the group consisting of inorganic pigments and organic pigments.

12. A magnetic fluid according to Claim 11, wherein said organic pigment is a phthalocyanine pigment.

FIG. 1

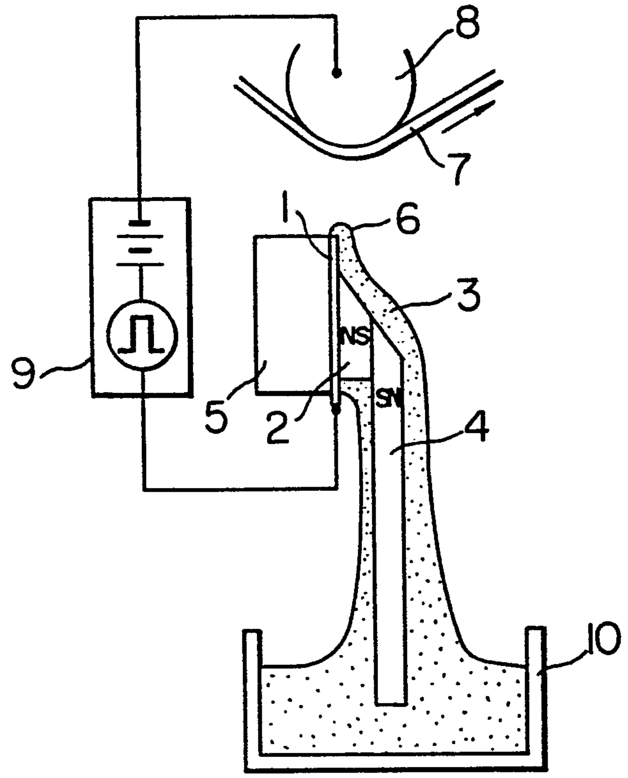

FIG. 2