

MICROCAPSULES FOR PRESSURE-SENSITIVE RECORDING PAPER
AND THE METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to microcapsules for use in the preparation of pressure-sensitive recording paper and a method for producing the same. More particularly, the invention relates to the microcapsules and the method for producing the same, which microcapsules have relatively large particle diameters and a narrow particle size distribution and are excellent in color developing property.

(2) Description of the Prior Art

Various kinds of pressure-sensitive recording materials are hitherto known well. For example, a colorless or a light colored electron-donative color forming agent (hereinafter referred to as "color former") is dissolved in a solvent and the obtained solution is formed into microcapsules. One surface of a sheet of paper is applied with these microcapsules. The surface of another sheet of paper is applied with a electron-acceptive substance (hereinafter referred to as "color developer") such as an acidic inorganic substance, a polymeric material, and aromatic carboxylic acids which produce a color upon reacting with the above color former. When the recording material is used, the treated surfaces of the above set of paper sheets

1 are put together face to face and local pressures are
2 applied to the paired sheets, thereby obtaining desired
3 duplicate impressions.

4 The recording mechanism in the pressure-sensitive
5 recording material of this type is such that the microcap-
6 sules applied on the surface of a sheet of paper are
7 ruptured by the pressure of handwriting or typewriting to
8 release the color former solution from microcapsules. The
9 solution containing a color former comes into contact with
10 the color developer on the opposing surface of the other
11 sheet of paper to produce a color.

12 There is also know anther type of recording paper
13 in which the respective coating materials providing such a
14 color forming mechanism are applied together to one surface
15 of a substrate paper.

16 Various methods for producing the microcapsules
17 for use in the preparation of pressure-sensitive recording
18 materials are hitherto proposed. For example, a solution of
19 a color former in a hydrophobic solvent is dispersed with a
20 dispersing agent and membranes of synthetic resin are formed
21 over the dispersed particles.

22 More particularly, in the method disclosed in
23 Japanese Laid-Open Patent Publication No. 54-85184, an
24 aqueous solution of a dispersing agent containing urea is
25 mixed with a color former solution to disperse the color
26 former solution and formaldehyde is added to the obtained

1 dispersion and the urea and formaldehyde are polymerized by
2 heating to form resin membranes over the dispersed
3 particles. Furthermore, disclosed in Japanese Laid-Open
4 Patent Publication No. 58-216737 is a method of producing
5 microcapsules in which a membrane forming agent and a
6 dispersing agent are dissolved in water to prepare an
7 aqueous solution of them, a hydrophobic solvent solution of
8 a color former is mixed into the above solution to be
9 dispersed and the obtained dispersion is heated to cause
10 thermal polymerization to form resin membranes over the
11 dispersed particles. In addition, there is a method of
12 producing microcapsules in which a primary condensation
13 product is obtained by reacting urea, melamine and
14 formaldehyde and a hydrophobic solvent containing this
15 condensation product and a color former are mixed with an
16 aqueous solution of dispersing agent to produce a dispersion
17 and the obtained dispersion is heated to form resin
18 membranes over the dispersed particles. In any of the
19 methods, the so-called in-situ polymerization is employed.

20 However, the particle diameters of microcapsules
21 prepared in the conventional methods are too small for use
22 as microcapsules in the preparation of pressure-sensitive
23 recording paper. Furthermore, the particle size distribu-
24 tion of the microcapsule is too wide, so that the color
25 developing property as the pressure-sensitive recording
26 paper is not always satisfactory.

1 Meanwhile, in order to prepare microcapsules
2 having a narrow particle size distribution, the diameter of
3 dispersed particles in the dispersed liquid of hydrophobic
4 solvent must be limited. However, the conventional methods
5 have not always been satisfactory in this regard.

6 BRIEF SUMMARY OF THE INVENTION

7 The present invention is intended to solve the
8 above-described problems in the prior art involved in the
9 pressure-sensitive recording material.

10 The principal objects of the present invention
11 are, therefore, to narrow the range of particle size distri-
12 bution of microcapsules and to provide the microcapsules for
13 use in the preparation of pressure-sensitive recording paper
14 which is excellent in the color developing property.

15 Another object of the invention is to provide an
16 improved method for producing the above-mentioned microcap-
17 sules for the pressure-sensitive recording paper.

18 Still a further object of the present invention is
19 to provide an O/W type emulsion of color former solution
20 which is suitable for preparing microcapsules for pressure-
21 sensitive recording paper and which is large in particle
22 diameter and narrow in particle size distribution.

23 In view of the above objects according to the
24 present invention, the inventors have carried out intensive
25 investigations and found out specific dispersing agents,
26 proper dispersing conditions and membrane forming agents

1 which are compatible with the dispersing agents. As a
2 result, it was made possible to improve the particle size
3 distribution which has been one of the problems in the
4 conventional method for producing the pressure-sensitive
5 recording material, thereby reducing the range of particle
6 size distribution, enlarging the particle diameter, and
7 providing microcapsules for preparing a pressure-sensitive
8 recording material having excellent color developing rate
9 and color density.

10 It is, therefore, a first aspect of the present
11 invention to provide microcapsules for pressure-sensitive
12 recording paper which is characterized in that the arith-
13 metical mean particle diameter of the microcapsules is in
14 the range of 3 to 10 μm and, in the cumulative particle size
15 distribution taken from the side of larger particles, the
16 ratio of the diameter at 25% value to the diameter at 50%
17 value is not more than 1.25 and the ratio of diameter at 75%
18 value to the diameter at 50% value is not less than 0.75 and
19 the standard deviation of the particle size distribution is
20 in the range of 1 to 2 μm .

21 "The diameter at 50% value in the cumulative
22 particle size distribution taken from the side of larger
23 particles" is the value on volume basis distribution and it
24 is hereinafter referred to simply as "50% diameter".

25 A second aspect of the present invention is the
26 microcapsules in the above first aspect in which the

1 microcapsules are those prepared by forming synthetic resin
2 membranes over the particles which are prepared by dispers-
3 ing a colorless or light colored electron-donative die
4 solution using a dispersing agent.

5 A third aspect of the present invention is the
6 microcapsules in the above second aspect in which the
7 dispersing agent is an isobutylene-maleic anhydride
8 copolymer or its modified product and the synthetic resin is
9 an amino resin.

10 The fourth aspect of the present invention is
11 that, in a method for producing microcapsules for pressure-
12 sensitive recording paper comprising the steps of dispersing
13 a colorless or light colored electron-donative color former
14 solution into water using a dispersing agent and forming
15 membranes of synthetic resin over the obtained dispersed
16 particles, the improvement in that the membranes are formed
17 over said dispersed particles which do not contain substan-
18 tially a membrane forming agent.

19 A further aspect of the present invention is an
20 O/W type emulsion of a solution of a colorless or light
21 colored electron-donative color former in a hydrophobic
22 solvent, which is characterized in that the arithmetical
23 mean particle diameter of said emulsion particles is in the
24 range of 3 to 10 μm and, in the cumulative particle size
25 distribution taken from the side of larger particles, the
26 ratio of the diameter at 25% value to the diameter at 50%

1 value is not more than 1.25 and the ratio of the diameter at
2 75% value to the diameter at 50% value is not less than 0.75
3 and the standard deviation of the particle size distribution
4 is in the range of 1 to 2 μm .

5 Still a further aspect of the present invention is
6 a method for producing an O/W type emulsion of the solution
7 of a colorless or light colored electron-donative color
8 former in a hydrophobic solvent, which comprises the steps
9 of mixing a colorless or light colored electron-donative
10 color former in a hydrophobic solvent with an aqueous
11 solution of dispersing agent to give an apparently uniform
12 state of mixture in a preliminary dispersing step, and then
13 vigorously stirring the mixture.

14 DETAILED DESCRIPTION OF THE INVENTION

15 This invention will be described in more detail in
16 the following.

17 The color former solution used in the method of
18 the present invention is prepared by dissolving an electron-
19 donative color former into a hydrophobic solvent such as
20 aromatic hydrocarbon solvent. The color former is not
21 especially limited, so that known compounds can be used.
22 For example, triarylmethane color formers, diphenylethane
23 color formers, thiazine color formers, spiropyran color
24 formers, and xanthene color formers, are used. More partic-
25 ularly, the color former is exemplified by Crystal Violet
26 Lactone and benzoyl Leucomethylene Blue.

1 The aromatic hydrocarbon solvents in the above
2 hydrophobic solvents are exemplified by diarylalkanes such
3 as phenylxylylethane, phenylethylphenylethane and butyl-
4 diphenylethane; alkyl naphthalenes such as diisopropyl-
5 naphthalene; and alkyl biphenyls such as monoisopropyl
6 biphenyl. Besides them, usable solvents are aliphatic
7 hydrocarbon solvents such as normal paraffin and isoparaf-
8 fin; alicyclic hydrocarbon solvents having a naphthene ring,
9 animal and vegetable oils such as fish oils, lard oil,
10 peanut oil, linseed oil, soybean oil, castor oil, and corn
11 oil. These materials can be used singly or in a mixture of
12 two or more.

13 The concentration of the color former is not
14 especially limited, however, it is generally in the range of
15 0.01 to 20% by weight. If necessary, heating can be done in
16 the dissolving of a color former.

17 The color former solution prepared by dissolving a
18 color former is then dispersed in water with a dispersing
19 agent. As the dispersing agent, a maleic anhydride copoly-
20 mer is used. The comonomers which are copolymerized with
21 maleic anhydride are exemplified by linear or branched
22 olefinic hydrocarbons such as ethylene, propylene, 1-butene,
23 1-pentene, 2-methyl-1-butene, 1-hexene, 2-methyl-1-pentene,
24 3-methyl-1-pentene, 2-ethyl-1-butene, and diisobutylene.
25 Among them, α -olefins are mainly used. Besides them, the
26 copolymers of styrene and methyl vinyl ether are also

1 usable. These materials are used either singly or in a
2 mixture of them.

3 In the present invention, it is preferable that
4 isobutylene-maleic anhydride copolymer is used as a dispers-
5 ing agent. The molecular weight of the copolymer is in the
6 range of about 50,000 to 300,000, and preferably in the
7 range of 10,000 to 200,000. The ratio of maleic anhydride
8 in the co-monomers is in the range of 20 to 60 molar %,
9 preferably in the range of 40 to 50 molar %. When
10 isobutylene and maleic anhydride are used, the equimolar
11 ratio is preferable. As far as the isobutylene and maleic
12 anhydride are copolymerized, modified compounds may be used
13 through a known process.

14 For the modification of these compounds, esterifi-
15 cation, amine modification and amide modification are
16 employed. Furthermore, it is possible to copolymerize
17 another co-monomer in the range that the water solubility of
18 the isobutylene-maleic anhydride copolymer is not impaired.
19 The co-monomers for this purpose are exemplified by the
20 above-mentioned styrene, methyl vinyl ether, and in
21 addition, acrylic acid and methacrylic acid and esters of
22 them with methanol, ethanol or butanol and amine- or amide-
23 modified co-monomer. In the use of these copolymers, the
24 quantity of maleic anhydride is preferably in the above-
25 described range.

26 In the dispersing process using isobutylene-maleic

1 anhydride copolymer, an aqueous solution of the isobutylene-
2 maleic anhydride copolymer is prepared. This aqueous
3 solution can easily be prepared by heating or by alkalifying
4 it. The concentration of the aqueous solution is in the
5 range of 1 to 20% by weight. If the concentration is lower
6 than 1% by weight, the dispersion takes a long time
7 resulting in a low production efficiency. On the other
8 hand, if the concentration is higher than 20% by weight, the
9 viscosity of the aqueous dispersing agent is raised which
10 causes difficulty in the formation of larger particles and a
11 narrow particle size distribution. Therefore, it is not
12 acceptable in view of the economy in production.

13 By mixing and stirring the color former solution
14 containing a dissolved color former and the aqueous solution
15 of isobutylene-maleic anhydride copolymer as a dispersing
16 agent, the O/W type emulsion can be prepared by dispersing
17 the color former solution. The mixing ratio of the color
18 former solution to the isobutylene-maleic anhydride solution
19 is preferably in the range of 20:1 to 5:1 by weight as solid
20 contents. If the ratio of color former solution is larger
21 than the above value of 20:1, the dispersing takes longer
22 time and the stability of dispersion is lowered. On the
23 other hand, if the ratio of color former solution is smaller
24 than the above value of 5:1, the dispersing effect is too
25 large which makes the controlling of particle size
26 difficult. In addition, a larger dispersing device must be

1 employed which increases the cost for the processing.

2 The temperature of dispersing is one of important
3 factors. The temperature is preferably in the range of 10
4 to 50°C, and more preferably 15 to 40°C. If the dispersing
5 temperature is too low, the fluidity of solutions in a
6 dispersing vessel is lowered, which exerts a bad influence
7 relative to the particle distribution. Therefore, it is not
8 possible to control the particle size and to narrow the
9 particle size distribution. In addition, if the temperature
10 is too high, the controlling of particle size is difficult
11 because the dispersing action is accelerated to excess and
12 bubbles are taken into the liquid, accordingly, the
13 stability of the dispersion is lost and a narrow particle
14 size distribution cannot be obtained.

15 The pH value in the dispersion depends upon the pH
16 value of the aqueous solution of dispersing agent, however,
17 a value in the range of 2.5 to 4.0 is preferable in the
18 usual operation.

19 The preferable stirrers for use in the dispersing
20 process are conventionally used homogenizers because the
21 handling of them is not difficult. As the homogenizer of
22 this sort is a cylindrical vessel having a certain volume
23 which is provided with an agitating blade, if necessary, a
24 plurality of agitating blades, in which the rotational speed
25 of the agitating blades and other operation conditions can
26 be optionally controlled. The shape of blade may be in the

1 form of a flat plate, a twisted plate, or in any other
2 appropriate shape.

3 With regard to the dispersing vessel, the shearing
4 diameter (the diameter of agitating blade) to the inner
5 diameter of the dispersing vessel, is preferably in the
6 range of 1:4-8. It is necessary to select a proper value
7 concerning the diameter of dispersing vessel. For example,
8 if the diameter is too large, the turbulence of fluid is
9 lowered and the particles in the vessel flow through
10 constant passages, as a result, large dispersion particles
11 in a wide particle size distribution are sometimes formed.
12 However, even when a large diameter vessel is used,
13 particles of proper diameters can be formed by additionally
14 using an auxiliary stirrer so as to attain uniform stirring.
15 On the other hand, when the diameter of a dispersing vessel
16 is too small, the turbulence of fluid is too large and air
17 bubbles are taken into the liquid phase.

18 Furthermore, the formation of dead spaces, i.e.,
19 the portions not moving, are liable to occur in the corner
20 of bottom portion of the dispersing vessel during the
21 stirring. In order to avoid the formation of such dead
22 spaces, it is desirable to make the bottom portion of dis-
23 persing vessel protruded downwards, such as in the shape of
24 an inverted cone or an inverted hemisphere, thereby enabling
25 to insert the stirring blades into the portion near the
26 bottom.

1 With regard to the rotational speed of the stirrer
2 in the dispersing vessel, the peripheral speed of stirring
3 blades is important. In general, in order to narrow the
4 particle size distribution and to reduce the time length of
5 operation, the peripheral speed is preferably in the range
6 of 12 to 22 m/sec. The peripheral speed can be calculated
7 with an equation of:

$$S = \pi d n / 60$$

8
9 in which S = peripheral speed (m/sec), d = diameter of
10 stirring blade (m) and n = rotational speed (rpm). In the
11 case of a small size apparatus, the rotational speed of a
12 stirrer is preferably in the range of 3,000 to 15,000 rpm.

13 As described above, the high speed rotation is
14 necessary for the dispersing operation. However, it is
15 desirable that a preliminary dispersing with a low speed
16 stirring is done in the initial stage with low speed stir-
17 ring because the two liquids are unevenly mixed in the
18 initial state. After that, high speed stirring is carried
19 out. When the preliminary dispersing is not sufficient, it
20 is impossible to obtain a narrow particle size distribution.
21 The preliminary dispersing is carried out with a rotational
22 speed generally in the range of 1,000 to 2,000 rpm and must
23 be continued to the condition that two liquids are roughly
24 mixed together. The time length for the preliminary
25 dispersing is generally 1 to 10 minutes and when the aqueous
26 solution and the solvents which were separated in the

1 initial stage, are mixed in an apparent state of almost
2 uniform dispersion, it is regarded that the preliminary
3 dispersing is finished.

4 After the preliminary dispersing, the color former
5 solution is further dispersed in water phase by the above-
6 mentioned high speed stirring. The time length for the
7 stirring is not especially limited, however, it is generally
8 in the range of 1 to 30 minutes.

9 Through the above-described process, the color
10 former solution is dispersed and the dispersion particles of
11 the color former solution are formed.

12 The method to disperse by mixing and stirring the
13 color former solution and the aqueous solution of dispersing
14 agent was described above. Besides the above method, it is
15 possible to employ optionally a process, for example, when
16 an aqueous solution of dispersing agent is prepared, a color
17 former solution is simultaneously added and stirred together
18 to prepare a dispersion. In any method, the color former
19 solution is dispersed in the first place with the aid of the
20 dispersing agent of isobutylene-maleic anhydride copolymer
21 to obtain an aqueous dispersion. As far as such an aqueous
22 dispersion is prepared, any of the methods can be employed.

23 The preferable and inevitable point in the method
24 for producing microcapsules for pressure-sensitive recording
25 paper according to the present invention is that the
26 membrane forming material as described later does not

1 coexist substantially in the above procedure to prepare the
2 dispersed particles. In the conventional art, as disclosed
3 in the examples of the foregoing two patent gazettes, at
4 least a part of membrane forming material coexists already
5 in the dispersed particles in the procedure to disperse the
6 color former solution for the reasons to simplify the
7 process and so forth. Especially, such a measure is often
8 taken when the dispersing agent of isobutylene-maleic
9 anhydride copolymer is used. It should be noted, however,
10 that if the membrane forming material exists in the stage to
11 obtain the dispersion particles, there is a possibility that
12 the polycondensation of the membrane forming material is
13 caused to proceed by the heat generated in the dispersing.
14 The occurrence of such polycondensation is not desirable
15 because the polymerization of the membrane forming material
16 itself and capsules containing gas bubbles occur. In
17 addition, the stability of dispersion particles is impaired
18 and it is sometimes difficult to prepare microcapsules
19 having a narrow particle size distribution by regulating the
20 particle diameter. Accordingly, it is desirable to prepare
21 an aqueous dispersion of color former solution without
22 substantially containing the membrane forming material.

23 Through the above procedure, it is possible to
24 prepare the O/W type emulsion of the hydrophobic solvent
25 solution of a colorless or light colored electron-donative
26 color former, in which the arithmetical mean particle

1 diameter is in the range of 3 to 10 μm and, in the
2 cumulative particle size distribution taken from the side of
3 larger particles, the ratio of the diameter at 25% value to
4 the diameter at 50% value is not more than 1.25 and the
5 ratio of the diameter at 75% value to the diameter at 50%
6 value is not less than 0.75 and the standard deviation of
7 the particle size distribution is in the range of 1 to 2 μm .

8 In the next step, synthetic resin membranes are
9 formed over the dispersion particles. The synthetic resins
10 used for this purpose are preferably the amino resins such
11 as melamine-formaldehyde resin and urea-formaldehyde resin.
12 The so-called in-situ polymerization is employed as the
13 method for the formation of membranes.

14 The amino resin can be prepared by the polyconden-
15 sation of formaldehyde and an amine having two amino groups
16 in the molecule such as urea, melamine, guanidine, N-methyl
17 urea, and thiourea. Those properly modified with polyphe-
18 nols such as resorcinol, catechol and pyrogallol and alcohol
19 such as butanol, can also be used.

20 In order to form the resin membranes over disper-
21 sion particles, it is possible to use the method to
22 polymerize the above synthetic resin membrane forming
23 material by mixing it into the above aqueous dispersion.
24 The usable membrane forming materials of synthetic resin are
25 exemplified by monomers of urea, melamine, formaldehyde. In
26 addition, the precondensates or modified products of

1 urea-formaldehyde (methylolurea), melamine-formaldehyde
2 (methylolmelamine) or urea-melamine-formaldehyde can also be
3 used. In the preparation of an aqueous solution of membrane
4 forming agent, a proper quantity of the dispersing agent of
5 above-mentioned isobutylene-maleic anhydride copolymer can
6 be added. The addition of this isobutylene-maleic anhydride
7 copolymer to the aqueous solution of membrane forming agent
8 is desirable for the reason that the formation of resin
9 membranes is accelerated and a part of the copolymer serves
10 as a membrane forming component.

11 The above-described polycondensation of an amine
12 with formaldehyde can be carried out through a well known
13 method. For example, it is preferable that the reaction
14 system of amine and formaldehyde is made alkaline. The
15 reaction temperature is in the range of 10 to 95°C, and
16 preferably 25 to 85°C. The molar ratio of formaldehyde to
17 amine such as urea is in the range of 0.6 to 5.0, preferably
18 1.0 to 4.0. The reaction time is selected from the range of
19 10 minutes to 10 hours.

20 Through the above-described process, the membranes
21 of synthetic resin are formed over the dispersion particles
22 of color former solution, thereby obtaining the microcap-
23 sules for the preparation of pressure-sensitive recording
24 paper.

25 The particle size distribution of microcapsules
26 which have hitherto been used for the pressure-sensitive

1 recording paper, is considerably wide. Accordingly, there
2 exist the capsules of larger particle size and those of
3 smaller particle size in comparison with a desirable range
4 in particle size. The capsules of excessively small
5 particle sizes are buried in the spaces among fibers of
6 substrate paper, in the binder for fixing capsules to the
7 substrate paper, or in the buffering agent to protect
8 capsules from the pressure of weight load or friction, so
9 that the smaller capsules cannot be ruptured or even when
10 they are ruptured, the color former solution does not run
11 out of capsules, therefore the excessively small capsules
12 cannot contribute to the development of color sometimes.
13 These cause the lowering of the rate and density of color
14 development. Furthermore, if the quantity of small capsules
15 is large, the use quantity of the membrane forming agent
16 must be increased because the surface area of capsules
17 increases.

18 On the other hand, in the case of capsules having
19 too large particle diameters, the resisting property to the
20 pressures of weight load and friction is lowered, so that
21 stains are caused to occur due to the partial color develop-
22 ment in the surface applied with a color developer, which is
23 difficulty used sometimes as a pressure-sensitive recording
24 paper.

25 It is generally accepted that the mean particle
26 diameter of capsules to be applied to upper paper of a

1 pressure-sensitive recording paper is preferably large. For
2 example, when microcapsules of large diameter containing a
3 color former solution of high concentration is used, much
4 color former is rapidly released to the surface of color
5 developer, so that the color developing is rapid and dense
6 to enable to prepare a pressure-sensitive recording paper of
7 high color density. Accordingly, it is considered that
8 microcapsules having a larger particle diameter is
9 desirable, however, if the particle diameter is too large,
10 the hydrophobic solvent containing a color former runs
11 widely to produce large blots, so that it is impossible to
12 produce clear images of characters. Accordingly, the arith-
13 metical mean particle diameter of the microcapsules for
14 pressure-sensitive recording paper in the present invention
15 is in the range of 3 to 10 μm , preferably in the range of 4
16 to 8 μm . When color developing property is regarded as
17 important, the particle diameter of capsules is made large.
18 Meanwhile, when the prevention of stain is regarded as
19 important, the particle diameter of capsules is made small.

20 Furthermore, an especially important point is that
21 the particle size distribution of microcapsules is narrow
22 (sharp). When the particle size distribution is narrow, the
23 a buffer agent suitable for the groups of particles is easy,
24 the use quantities of buffer agent and binder are small, and
25 the staining of under paper is reduced, thereby enabling to
26 produce a pressure-sensitive recording paper with excellent

1 color developing property.

2 In view of the above facts, the following stand-
3 ards are set, that is, in the cumulative particle size
4 distribution taken from the side of larger particles, the
5 ratio of the diameter at 25% value to the diameter at 50%
6 value is not more than 1.25, that is in the range of 1.00 to
7 1.25 and the ratio of the diameter at 75% value to the
8 diameter at 50% value is not less than 0.75, that is 0.75 to
9 1.00, and the standard deviation of the particle size
10 distribution is in the range of 1 to 2 μ m. When these
11 conditions are met, the particle size distribution is narrow
12 and it is possible to produce microcapsules for pressure-
13 sensitive recording paper which is economical and is
14 excellent in color developing property. The above particle
15 diameters corresponding to the respective cumulative
16 percentages are measured by particle groups using Coulter
17 Counter (trademark, made by Coulter K.K.) The value of
18 standard deviation is also obtained by the same test
19 machine.

20 The microcapsules for pressure-sensitive recording
21 material consisting of the particle groups having a narrow
22 particle size distribution can easily be prepared through a
23 method using a dispersing agent of isobutylene-maleic
24 anhydride copolymer.

25 That is, when the O/W type emulsion of color
26 former solution is prepared, the obtained emulsion produces

1 basically an influence to the final shape of microcapsules.
2 Accordingly, when the above microcapsules are produced,
3 those having an arithmetical mean particle diameter in the
4 range of 3 to 10 μm and, in the cumulative particle size
5 distribution taken from the side of larger particles, the
6 ratio of the diameter at 25% value to the diameter at 50%
7 value of not more than 1.25 and the ratio of the diameter at
8 75% value to the diameter at 50% value of not less than 0.75
9 and the standard deviation of the particle size distribution
10 in the range of 1 to 2 μm , must be used.

11 A proper quantity of an ordinary binder is added
12 to the thus obtained dispersion of microcapsules and the
13 dispersion is applied to a substrate paper and it is then
14 subjected to drying to produce pressure-sensitive recording
15 paper with microcapsules.

16 In the following, the present invention is
17 described in more detail with reference to several examples.

18 EXAMPLE

19 Microcapsules were prepared using several kinds of
20 dispersing agents in the following preparation examples. The
21 particle size distributions of the microcapsules were
22 measured and evaluated by comparing to one another.

23 Described in the first place are the cases in
24 which any membrane forming agent is not used in dispersing
25 processes.
26

1 <Preparation Example 1>

2 (Dispersing Step)

3 The preparation of a hydrophobic solution of color
4 former and an aqueous solution of dispersing agent was
5 carried out through the following method.

6 (1) Preparation of Hydrophobic Solution of Color former

7 A solvent mixture (100 weight parts) of phenyl-
8 xylyl phenylethane and phenylethyl phenylethane as a
9 hydrophobic solvent and 5 weight parts of Crystal Violet
10 Lactone (CVL) as a color former were put into a beaker. The
11 contents were heated to 120°C with stirring to dissolve the
12 color former. After that, the solution was cooled to a
13 temperature of 35°C to obtain a color former solution.

14 (2) Preparation of Aqueous Solution of Dispersing Agent

15 A ca. 22 wt.% aqueous solution (261 weight parts)
16 of isobutylene-maleic anhydride copolymer (trade name:
17 CHIOPET E-20, made by Chiyoda Petroleum Co., Ltd.) as a
18 dispersing agent and 528 weight parts of water were mixed
19 together to obtain an aqueous solution of dispersing agent.

20 (3) Dispersing Operation

21 A separable flask of about 2,000 ml was put in a
22 water bath and it was maintained at 40°C. A high speed
23 stirrer (trade name: TK HOMOMIXER MARK, made by Tokushu Kika
24 Kogyo Co., Ltd.) was put in the separable flask. The whole
25 quantities of previously prepared hydrophobic solution of
26 color former and aqueous solution of dispersing agent were

1 fed into the separable flask and a flat plate was set near
2 the liquid surface to avoid the splashing. After the liquid
3 temperature was raised to 38°C, the stirring was continued
4 for a while at a rotation rate of 1,800 rpm. After the
5 preliminary stirring in which a turbid state was observed by
6 naked eyes, the rotational speed was raised to 10,000 rpm
7 without delay. The temperature of the water bath was
8 controlled so as to prevent the temperature of dispersed
9 liquid did not rise above 40°C. Through the above-described
10 operation, a dispersed liquid of about 5 μ m in mean particle
11 diameter was prepared.

12 A small quantity of the obtained dispersed liquid
13 was sampled for test and it was diluted to 1/10 to 1/100
14 concentration in an electrolytic solution. The particle
15 size distribution was measured using a Coulter counter TA-II
16 (trade name, made by Coulter K.K.) with an orifice of 50 μ m
17 in diameter. The results are shown in Table 1.

18 (Capsulation Step)

19 (1) Preparation of Membrane Forming Agent

20 To a 300 ml beaker were added 44 weight parts of
21 urea (reagent grade, above 99% purity) and 19 weight parts
22 of melamine (reagent grade, above 99% purity). Then, 143
23 weight parts of 37% aqueous solution of formaldehyde was
24 added and the reaction was carried out for 20 minutes in a
25 water bath at 60°C with stirring. After the reaction, the
26 reaction mixture was cooled to 35°C to obtain a preliminary

condensation product as a membrane forming agent.

(2) Capsulation Operation

The previously prepared dispersed liquid was put into the separable flask which was used in the dispersing operation and it was stirred using an ordinary stirrer. The whole of the membrane forming agent was poured gradually into the flask along its inlet wall. The separable flask was put in a warm water bath at 60°C. The preliminary condensation product of melamine-urea-formaldehyde was reacted for 3 hours after the liquid temperature was raised to 60°C to form melamine-urea-formaldehyde resin membranes over the dispersion particles. After stopping the heating, the stirring was continued for about 10 hours. After that, about 24 weight parts of 28% aqueous ammonia was added with stirring and about 7.5 weight parts of 20% aqueous solution of sodium hydroxide to adjust the pH to 9 so as to prepare microcapsules. The particle size distribution of the obtained microcapsules was measured, the result of which is shown in Table 1.

<Preparation Example 2>

(Dispersing Step)

(1) Preparation of Hydrophobic Solution of Color Former

A hydrophobic solution of color former was prepared in the like manner as in Preparation Example 1.

(2) Preparation of Aqueous Solution of Dispersing Agent

An aqueous solution of dispersing agent was

1 prepared in the like manner as in Preparation Example 1
2 except that 129 weight parts of CHIOPET E-20 and 458 weight
3 parts of water were used.

4 (3) Dispersing Operation

5 A dispersed liquid was prepared in the like manner
6 as in Preparation Example 1 using the above obtained hydro-
7 phobic solution of color former and the aqueous solution of
8 dispersing agent, in which the mean particle diameter was
9 about 5 μ m. Its particle size distribution was measured,
10 the results of which are shown in Table 1.

11 (Capsulation Step)

12 (1) Preparation of Membrane Forming Agent

13 To a 500 ml beaker were added 203 weight parts of
14 60 wt.% aqueous solution of methylolmelamine (trade name:
15 SUMITEX RESIN M-3, made by Sumitomo Chemical Co., Ltd.), 45
16 weight parts of CHIOPET E-20 and 167 weight parts of water,
17 and they were mixed together with stirring to obtain a
18 membrane forming agent.

19 (2) Capsulation Operation

20 Through the process in the like manner as in
21 Preparation Example 1, microcapsules which was finally
22 adjusted to pH 9 was obtained. The particle size distribu-
23 tion of the obtained microcapsules was measured, the results
24 of which are shown in Table 1.

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1 <Preparation Example 3>

2 (Dispersing Step)

3 (1) Preparation of Hydrophobic Solution of Color Former

4 A hydrophobic solution of color former was
5 prepared in the like manner as in Preparation Example 1.

6 (2) Preparation of Aqueous Solution of Dispersing Agent

7 An aqueous solution of dispersing agent was
8 prepared by mixing 260 weight parts of methyl vinyl ether-
9 maleic anhydride copolymer (trade name: AN-119 BF, made by
10 GAF Corporation) and 530 weight parts of water.

11 (3) Dispersing Operation

12 A dispersed liquid was prepared in the like manner
13 as in Preparation Example 1 except that the rotational speed
14 in dispersing was 7,500 rpm and the particle size
15 distribution was measured, the results of which are shown in
16 Table 1.

17 (Capsulation Step)

18 (1) Preparation of Membrane Forming Agent

19 Using melamine-urea-formaldehyde preliminary
20 condensation product in the like manner as in Preparation
21 Example 1 and 6 weight parts of resorsinol (made by Kishida
22 Chemical Co., Ltd.) was mixed to obtain a membrane forming
23 agent.

24 (2) Capsulation Operation

25 Through the process in the like manner as in
26 Preparation Example 1, microcapsules which was finally

adjusted to pH 9 was obtained. The particle size distribution of the obtained microcapsules was measured, the results of which are shown in Table 1.

T a b l e 1

Preparation Examples	Dispersing Agent		Mean Particle Diameter (μm)	Standard Deviation (μm)	Ratio of Diameter	
	Kind	MFA ⁽¹⁾			25%D.	75%D.
					50%D.	50%D.
[After Emul- sification]						
Prep.Ex. 1	IB-MA ⁽²⁾	No	5.0	1.3	1.18	0.82
Prep.Ex. 2	IB-MA	No	5.0	1.2	1.16	0.82
Prep.Ex. 3	MVE-MA ⁽³⁾	No	4.9	2.2	1.33	0.69
[After Capsulation]						
Prep.Ex. 1	--	--	5.3	1.3	1.16	0.81
Prep.Ex. 2	--	--	5.2	1.2	1.15	0.82
Prep.Ex. 3	--	--	5.4	2.9	1.37	0.67

Notes:

- (1) MFA: Existence of membrane forming agent
 (2) IB-MA: Isobutylene-maleic anhydride copolymer
 (3) MVE-MA: Methyl vinyl ether-maleic anhydride copolymer

As will be understood in view of Table 1, the particle size distributions of the dispersed liquids and the microcapsules in Preparation Examples 1 and 2 were narrower than those in Preparation Example 3. Furthermore, the agglomeration was not observed in Preparation Examples 1 and 2 because the compatibility between the dispersing agent and membrane forming agent was good, so that the values in particle size distributions of the dispersed liquids and the microcapsules were the same and desirable microcapsules were prepared.

In the following, the cases in which the membrane forming agent was added during the dispersing step will be described.

<Preparation Example 4>

(Dispersing Step)

(1) Preparation of Hydrophobic Solution of Color former

A hydrophobic solution of color former was prepared in the like manner as in Preparation Example 1.

(2) Preparation of Aqueous Solution of Dispersing Agent

An aqueous solution of dispersing agent was prepared in the like manner as in Preparation Example 1.

(3) Preparation of Membrane Forming Agent

A membrane forming agent was prepared in the like manner as in Preparation Example 1.

(4) Dispersing Operation

A separable flask of about 2,000 ml was put in a

1 water bath and it was maintained at 15°C. A high speed
2 stirrer (trade name: TK HOMOMIXER MARK, made by Tokushu Kika
3 Kogyo Co., Ltd.) was put in the separable flask. The whole
4 quantities of previously prepared hydrophobic solution of
5 color former and the aqueous solution of dispersing agent
6 were fed into the separable flask and the membrane forming
7 agent was further added. A flat plate was set near the
8 liquid surface to avoid the splashing. After the liquid
9 temperature reached 15°C, the stirring was continued for a
10 while at a rotation rate of 1,800 rpm. After the mixing,
11 the rotational speed was raised to 10,000 rpm rapidly. The
12 temperature of the water bath was controlled so as to
13 prevent the temperature of dispersed liquid did not rise
14 above 15°C. Through the above-described operation, a
15 dispersed liquid of about 5 μ m in the mean particle diameter
16 was obtained.

17 With regard to the obtained dispersed liquid, the
18 particle size distribution was measured in the like manner
19 as in Preparation Example 1. The results are shown in Table
20 2.

21 (Capsulation Step)

22 (1) Capsulation Operation

23 The previously prepared dispersed liquid contain-
24 ing the membrane forming agent was put into a separable
25 flask and it was stirred using an ordinary stirrer. The
26 separable flask was put in a warm water bath at 60°C. The

1 reaction was carried out for 3 hours with regulating the
2 temperature to 60°C to form melamine-urea-formaldehyde resin
3 membranes over the dispersion particles. After stopping the
4 heating, the stirring was continued for about 10 hours.
5 After that, about 24 weight parts of 28% aqueous ammonia was
6 added with stirring and about 7.5 weight parts of 20%
7 aqueous solution of sodium hydroxide was added to adjust the
8 pH to 9 so as to prepare microcapsules. The particle size
9 distribution of the obtained microcapsules were measured,
10 the result of which is shown in Table 2.

11 <Preparation Example 5>

12 (Dispersing Step)

13 A hydrophobic solution of color former, a hydro-
14 phobic solution of dispersing agent and a membrane forming
15 agent were prepared in the like manner as in Preparation
16 Example 2. Then, the dispersing operation was carried out
17 in the co-existence of the membrane forming agent in the
18 like manner as in Preparation Example 4 to obtain a
19 dispersed liquid. With regard to the obtained dispersed
20 liquid, the particle size distribution was measured and the
21 results are shown in Table 2.

22 (Capsulation Step)

23 The capsulation was carried out in the like manner
24 as in Preparation Example 4 to prepare microcapsules that
25 was finally adjusted to pH 9. The particle size distribu-
26 tion of the obtained microcapsules were measured, the result

1 of which is shown in Table 2.

2 <Preparation Example 6>

3 The preparation process was carried out in the
4 like manner as in Preparation Example 4 except that a
5 dispersing agent of methyl vinyl ether-maleic anhydride
6 copolymer (trade name: AN-119 BF, made by GAF Corporation)
7 was used to prepare microcapsules that was finally adjusted
8 to pH 9. The particle size distribution of the obtained
9 microcapsules were measured, the result of which is shown in
10 Table 2.

11 <Preparation Example 7>

12 The preparation process was carried out in the
13 like manner as in Preparation Example 4 except that a
14 dispersing agent of α -methylstyrene-maleic anhydride
15 copolymer (trade name: SUMIREZ RESIN DS-40K, made by
16 Sumitomo Chemical Co., Ltd.) was used to prepare micro-
17 capsules that was finally adjusted to pH 9. The particle
18 size distribution of the obtained microcapsules were
19 measured, the result of which is shown in Table 2.
20
21
22
23
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T a b l e 2

Preparation Examples	Dispersing Agent		Mean Particle Diameter (μ m)	Standard Deviation (μ m)	Ratio of Diameter	
	-----				25%D.	75%D.
	Kind	MFA ⁽¹⁾			50%D.	50%D.
[After Emul- sification]						
Prep.Ex. 4	IB-MA ⁽²⁾	Yes	5.0	1.6	1.22	0.77
Prep.Ex. 5	IB-MA	Yes	5.1	1.6	1.22	0.76
Prep.Ex. 6	MVE-MA ⁽³⁾	Yes	5.0	2.1	1.31	0.70
Prep.Ex. 7	St-MA ⁽⁴⁾	Yes	5.8	2.4	1.27	0.73
[After Capsulation]						
Prep.Ex. 4	--	--	5.2	1.6	1.21	0.78
Prep.Ex. 5	--	--	5.2	1.7	1.22	0.77
Prep.Ex. 6	--	--	5.0	2.2	1.32	0.69
Prep.Ex. 7	--	--	5.9	2.3	1.29	0.75

Notes:

- (1) MFA: Existence of membrane forming agent
 (2) IB-MA: Isobutylene-maleic anhydride copolymer
 (3) MVE-MA: Methyl vinyl ether-maleic anhydride copolymer
 (4) St-MA: α -Methylstyrene-maleic anhydride copolymer

1 As will be understood in view of Table 2, the
2 particle size distributions of the dispersed liquids and the
3 microcapsules in Preparation Examples 4 and 5 were very
4 narrow as compared with those in Preparation Examples 6 and
5 7. Furthermore, the agglomeration or partial separation was
6 not observed because the compatibility between the dispers-
7 ing agent and the membrane forming agent is good, so that no
8 difference in the particle size distributions between the
9 dispersed liquid and the microcapsule was observed and
10 desirable microcapsules were prepared.

11 The influence to the color developing property
12 which was brought about by the difference in particle
13 diameters of microcapsules was tested.

14 <Preparation Example 8>

15 A sizing agent and a protective agent were added
16 to microcapsules of about 5 μ m in particle size as prepared
17 in the same method as in Preparation Example 1 and it was
18 applied on a quality paper using a Mayer bar to prepare an
19 upper sheet of pressure-sensitive recording material.

20 In order to test the color developing property of
21 the pressure-sensitive recording paper, the above upper
22 sheet was put on a commercially available lower sheet to
23 which a color developer of salicylic acid compound was
24 previously applied. The color development was done using an
25 impact printer. The reflectance ratios of the lower sheet
26 were measured using a spectrophotometer at 3 seconds, 20

seconds and 60 minutes after the color development. The results of the measurement are shown in Table 3.

<Preparation Example 9>

Using the microcapsules of about 3 μm in particle size as prepared in the like manner as in Preparation Example 1 and an upper sheet of pressure-sensitive recording material was prepared in the like manner as in Preparation Example 8, and also in the similar manner, the color developing property was tested. The results of the test are shown in Table 3.

T a b l e 3

Preparation Examples	Mean Particle Diameter (μm)	Color Density (%)		
		After 3 sec.	After 20 sec.	After 60 min.
[After Capsulation]				
Prep.Ex. 8	5.4	79	85	87
Prep.Ex. 9	2.9	76	82	85

1 As will be understood in view of results in Table
2 3, the microcapsules having a larger mean diameter in
3 Preparation Example 8 excel in the color developing property
4 because both the initial color density and the final color
5 density of them are high as compared with those in Prepara-
6 tion Example 9.

7 In addition, it was ascertained that the upper
8 sheet prepared with the microcapsules obtained in
9 Preparation Example 8, did not stain the lower sheet by the
10 rupture of microcapsules and used as a pressure-sensitive
11 recording paper
12 of good quality.

13 Furthermore, in view of the results in Tables 1
14 and 2, it was understood that the microcapsules of
15 Preparation Examples 1 and 2 in which the coexistence of
16 membrane forming agent did not adopted during the dispersing
17 operation, had narrower particle size distributions as
18 compared with those in Preparation Examples 4 and 5 in which
19 the membrane forming agent was used together in the dispers-
20 ing. Accordingly, it is desirable that the dispersing
21 operation is carried out without the addition of the
22 membrane forming agent.

23 The microcapsules according to the present inven-
24 tion are characterized in the following points:

25 (1) The strength of microcapsules is large and the
26 microcapsules are hardly ruptured by pressures of loads and

friction in the uses.

(2) The agglomeration of microcapsules hardly occurs.

(3) The color is white or slightly colored.

(4) The particle size distribution is narrow.

(5) The particle diameter is relatively large.

(6) The storage stability of microcapsules is high.

(7) The color developing reaction in pressure-sensitive recording paper is not impaired and the rate of color development is high.

(8) The blurring of developed image in pressure-sensitive recording paper does not occur and clear images can be produced after the storage of a long period.

(9) Capsulation can be done without difficulty.

(10) Inexpensive.



1 WHAT IS CLAIMED IS:

2
3 1. Microcapsules for pressure-sensitive recording
4 paper which is characterized in that the arithmetical mean
5 particle diameter of said microcapsules is in the range of 3
6 to 10 μm and, in the cumulative particle size distribution
7 taken from the side of larger particles, the ratio of the
8 diameter at 25% value to the diameter at 50% value is not
9 more than 1.25 and the ratio of the diameter at 75% value to
10 the diameter at 50% value is not less than 0.75 and the
11 standard deviation of the particle size distribution is in
12 the range of 1 to 2 μm .

13
14 2. The microcapsules for pressure-sensitive
15 recording paper as claimed in Claim 1, wherein said
16 microcapsules are prepared by forming synthetic resin
17 membranes over the particles which are prepared by
18 dispersing a colorless or light colored electron-donative
19 die solution using a dispersing agent.

20
21 3. The microcapsules for pressure-sensitive
22 recording paper as claimed in Claim 2, wherein said
23 dispersing agent is an isobutylene-maleic anhydride
24 copolymer or its modified product and said synthetic resin
25 is an amino resin.
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1 4. In a method for producing microcapsules for
2 pressure-sensitive recording paper comprising the steps of
3 dispersing a colorless or light colored electron-donative
4 color former solution into water using a dispersing agent
5 and forming membranes of synthetic resin over the obtained
6 dispersion particles, the improvement comprises that said
7 membranes are formed over said dispersion particles which do
8 not contain substantially a membrane forming agent.

9
10 5. An O/W type emulsion of solution of a color-
11 less or light colored electron-donative color former in a
12 hydrophobic solvent, which is characterized in that the
13 arithmetical mean particle diameter of dispersion particles
14 is in the range of 3 to 10 μm and, in the cumulative
15 particle size distribution taken from the side of larger
16 particles, the ratio of the diameter at 25% value to the
17 diameter at 50% value is not more than 1.25 and the ratio of
18 the diameter at 75% value to the diameter at 50% value is
19 not less than 0.75 and the standard deviation of the
20 particle size distribution is in the range of 1 to 2 μm .

21
22 6. The O/W type emulsion as claimed in Claim 5,
23 wherein said emulsion is dispersed with a dispersing agent
24 of an isobutylene-maleic anhydride copolymer or its modified
25 product.

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1 7. A method for producing O/W type emulsion of
2 the solution of a colorless or light colored electron-
3 donative color former in a hydrophobic solvent, which
4 comprises the steps of mixing a colorless or light colored
5 electron-donative color former in a hydrophobic solvent with
6 an aqueous solution of dispersing agent to give an
7 apparently uniform mixed state in a preliminary dispersing
8 step, and then vigorously stirring the mixture.

9
10 8. The method for producing O/W type emulsion of
11 the solution of a colorless or light colored electron-
12 donative color former in a hydrophobic solvent as claimed in
13 claim 7, wherein said aqueous solution of dispersing agent
14 is an aqueous solution of isobutylene-maleic anhydride
15 copolymer or its modified product.

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