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(72) Inventeurs/Inventors:
YOSHINAKA, MASATOYO, JP;
KOBAYASHI, SHINJI, JP;
MORIMITSU, YUICHIRO, JP
(73) Propriétaire/Owner:
SUMITOMO SEIKA CHEMICALS CO., LTD., JP
(74) Agent: KIRBY EADES GALE BAKER

(54) Titre : COPOLYMERE HYDROSOLUBLE AYANT UN GROUPE CARBOXYLE MODIFIE AVEC UN GROUPE
ALKYLE

(54) Title: WATER-SOLUBLE COPOLYMER HAVING ALKYL-MODIFIED CARBOXYL GROUPS

(57) **Abrégé/Abstract:**

The present invention provides a water-soluble copolymer having alkyl-modified carboxyl groups which is able to produce a neutralized viscous liquid in which although its viscosity is very low when no electrolyte exists, the viscosity greatly increases when electrolytes are added, which has a sufficiently high viscosity and a very high transmittance and which has moist textures without stickiness even in the presence of a relatively high concentration of electrolytes, and a thickening agent comprising the same. More specifically, the present invention provides a water-soluble copolymer having alkyl-modified carboxyl groups which is obtained by polymerizing 100 parts by weight of (meth)acrylic acid, 5-10 parts by weight of lauryl (meth)acrylate, and 0-0.1 parts by weight of a compound having two or more ethylenic unsaturated groups, wherein a 1 weight %-neutralized viscous liquid shows a viscosity of 1000 mPa·s or lower and a transmittance of 95 % or higher, and when 1-7 parts by weight of sodium chloride is added to 100 parts by weight of the neutralized viscous liquid, the liquid shows a highest viscosity of 10000-30000 mPa·s and a transmittance of 95 % or higher, and a thickening agent comprising the same.

Abstract

The present invention provides a water-soluble copolymer having alkyl-modified carboxyl groups which is able to produce a neutralized viscous liquid in which
5 although its viscosity is very low when no electrolyte exists, the viscosity greatly increases when electrolytes are added, which has a sufficiently high viscosity and a very high transmittance and which has moist textures without stickiness even in the presence of a relatively
10 high concentration of electrolytes, and a thickening agent comprising the same. More specifically, the present invention provides a water-soluble copolymer having alkyl-modified carboxyl groups which is obtained by polymerizing
15 100 parts by weight of (meth)acrylic acid, 5-10 parts by weight of lauryl (meth)acrylate, and 0-0.1 parts by weight of a compound having two or more ethylenic unsaturated groups, wherein a 1 weight %-neutralized viscous liquid shows a viscosity of 1000 mPa·s or lower and a transmittance of 95 % or higher, and when 1-7 parts by
20 weight of sodium chloride is added to 100 parts by weight of the neutralized viscous liquid, the liquid shows a highest viscosity of 10000-30000 mPa·s and a transmittance of 95 % or higher, and a thickening agent comprising the same.

Water-soluble copolymer
having alkyl-modified carboxyl groups

Technical Field

5 [0001]

The present invention relates to a water-soluble copolymer having alkyl-modified carboxyl groups. More specifically, the present invention relates to a water-soluble copolymer having alkyl-modified carboxyl groups,
10 which may be preferably used as a thickening agent for cosmetics and the like.

Background

[0002]

15 A variety of copolymers are known as copolymers of (meth)acrylic acid and alkyl (meth)acrylate, which are used in thickening agents for cosmetics and the like; moisturizers for cataplasms and the like; emulsifiers; suspension stabilizers for suspensions; and the like. For
20 example, a copolymer obtained by reacting a specific amount of olefin-based unsaturated carboxylic acid monomers and a specific amount of alkyl (meth)acrylate (number of carbon atoms in the alkyl group is 10-30) (See Patent Document 1),
a copolymer obtained by reacting a specific amount of
25 olefin-based unsaturated carboxylic acid monomers and a specific amount of alkyl (meth)acrylate (number of carbon

atoms in the alkyl group is 10-30) and a cross linking agent
(See Patent Document 2), a copolymer obtained by reacting
olefin-based unsaturated carboxylic acid monomers and alkyl
(meth)acrylate (number of carbon atoms in the alkyl group is
5 8-30) (See Patent Document 3) and the like are known.

These copolymers of (meth)acrylic acid and alkyl
(meth)acrylate are used in the above applications usually
after dissolving into water and the like and neutralize
with alkali to form a neutralized viscous liquid at a
10 concentration of about 0.1 to 1 weight %.

[0003]

This neutralized viscous liquid had a problem that its
viscosity or transmittance is reduced and a part of the
copolymer precipitates when electrolytes used as various
15 raw materials for products or additives coexist even at
relatively low concentrations.

[0004]

In particular, recently, in the field of cosmetics and
the like, cosmetics containing high amounts of minerals and
20 the like in order to differentiate from other products as
well as various properties, for example, good appearances
such as transparency, non-sticky texture and the like are
in the spotlight. Therefore, it is desired to invent a
thickening agent which can form a neutralized viscous
25 liquid having a high viscosity and a high transmittance
even in the presence of a relatively high concentration of

electrolytes.

[0005]

[Patent Document 1] JP 6190/1976A

[Patent Document 2] JP 232107/1984A

5 [Patent Document 3] US 5004598

Disclosure of the Invention

[0006]

10 An object of the present invention is to provide a water-soluble copolymer having alkyl-modified carboxyl groups which is able to produce a neutralized viscous liquid which has a sufficiently high viscosity and a very high transmittance and which has moist textures without stickiness even in the presence of a relatively high
15 concentration of electrolytes, and a thickening agent containing the same.

[0007]

The present invention relates to, as will be described, a water-soluble copolymer having alkyl-modified carboxyl
20 groups.

[0008]

(1) A water-soluble copolymer having alkyl-modified carboxyl groups which is obtained by polymerizing 100 parts by weight of (meth)acrylic acid, 5-10 parts by weight of lauryl (meth)acrylate, and 0.001-0.044 parts by weight of a
25 compound having two or more ethylenic unsaturated groups,

wherein a 1 weight %-neutralized viscous liquid shows a viscosity of 1000 mPa·s or lower and a transmittance of 95 % or higher, and when 1-7 parts by weight of sodium chloride is added to 100 parts by weight of the neutralized viscous liquid, the liquid shows a highest viscosity of 10000-30000 mPa·s and a transmittance of 95 % or higher, wherein the 1 weight %-neutralized viscous liquid is a liquid containing 1 weight % of said water-soluble copolymer having alkyl-modified carboxyl groups which has been neutralized with an alkali.

[0009]

(2) The water-soluble copolymer having alkyl-modified carboxyl groups according to (1), wherein the compound having two or more of ethylenic unsaturated groups is at least one selected from a group consisting of pentaerythritol allyl ether, diethylene glycol diallyl ether, polyethylene glycol diallyl ether and polyallyl saccharose.

[0010]

(3) A thickening agent comprising the water-soluble copolymer having alkyl-modified carboxyl groups according to (1) or (2).

[0011]

The present invention will be explained in detail below.

4a

[0012]

Additionally, in the present invention, acrylic acid and methacrylic acid are inclusively described as (meth)acrylic acid.

5 [0013]

Further, in the present invention, neutralization for

the neutralized viscous liquid is to make the pH of the liquid 6.5-7.5.

[0014]

In the present invention, the water-soluble copolymer having alkyl-modified carboxyl groups is obtained by polymerizing (meth)acrylic acid and lauryl (meth)acrylate and optionally a compound having two or more of ethylenic unsaturated groups.

[0015]

When (meth)acrylic acid and lauryl (meth)acrylate are combined in the present invention, either or both of (meth)acrylic acid and lauryl (meth)acrylate may be used alone or in a combination of two or more, respectively. Among these combinations, a combination of acrylic acid and lauryl methacrylate is preferably used because they are easily treated due to liquid at room temperature and viscosity properties and transmittances are excellent regarding neutralized viscous liquids of the water-soluble copolymer having alkyl-modified carboxyl groups obtained therefrom and the liquids in the presence of electrolytes.

[0016]

The amount of lauryl (meth)acrylate used in the present invention is 5-10 parts by weight, more preferably 6-9.1 parts by weight with respect to 100 parts by weight of (meth)acrylic acid. When the amount of lauryl (meth)acrylate is less than 5 parts by weight with respect

to 100 parts by weight of (meth)acrylic acid, it is possible that a viscosity in the presence of electrolyte of a neutralized viscous liquid of the obtained water-soluble copolymer having alkyl-modified carboxyl groups is insufficient, while when the amount is more than 10 parts by weight, it is possible that water-solubility of the obtained water-soluble copolymer having alkyl-modified carboxyl groups deteriorates.

[0017]

10 The compounds having two or more of ethylenic unsaturated groups optionally used in the present invention are not especially limited but compounds in which the ethylenic unsaturated groups are allyl groups are preferable. Among them, pentaerythritol allyl ether such
15 as pentaerythritol diallyl ether, pentaerythritol triallyl ether, pentaerythritol tetraallyl ether and the like, diethylene glycol diallyl ether, polyethylene glycol diallyl ether and polyallyl saccharose are more preferable. These compounds having two or more of ethylenic unsaturated
20 groups may be used alone or in combination of two or more of them.

[0018]

 The amount of the compound having two or more of ethylenic unsaturated groups used in the present invention
25 is 0.001-0.1 parts by weight, more preferably 0.001-0.044 parts by weight with respect to 100 parts by weight of

(meth)acrylic acid. When the amount of the compound having two or more of ethylenic unsaturated groups is more than 0.1 parts by weight, it is possible that a transmittance in the presence of electrolyte of a neutralized viscous liquid of the obtained water-soluble copolymer having alkyl-modified carboxyl groups deteriorates or the liquid becomes clouded.

[0019]

In the present invention, a method for obtaining the water-soluble copolymer having alkyl-modified carboxyl groups by polymerizing (meth)acrylic acid and 5-10 parts by weight of lauryl (meth)acrylate with respect to 100 parts by weight of (meth)acrylic acid and optionally 0-0.1 parts by weight of a compound having two or more of ethylenic unsaturated groups with respect to 100 parts by weight of (meth)acrylic acid is not especially limited but ordinary methods such as a method for polymerizing these materials by stirring them in a solvent under an inactive gas atmosphere in the presence of a polymerization initiator and the like may be used.

[0020]

Inactive gases for producing an inactive gas atmosphere include, for example, a nitrogen gas, an argon gas and the like.

The aforementioned solvent is not especially limited insofar as they dissolve (meth)acrylic acid, lauryl

(meth)acrylate and a compound having two or more of ethylenic unsaturated groups but not the obtained water-soluble copolymer having alkyl-modified carboxyl groups and do not inhibit a polymerization reaction.

5 Examples of such a solvent include, for example, normal pentane, normal hexane, normal heptane, cyclopentane, cyclohexane and the like. Among them, normal hexane and normal heptane are preferably used.

[0021]

10 The amount of the solvent to be used is preferably 300-5000 parts by weight with respect to 100 parts by weight of (meth)acrylic acid from viewpoints of improving stirring workability and economy.

[0022]

15 The aforementioned polymerization initiator is preferably a radical polymerization initiator for example, α, α' -azoisobutyronitrile, 2,2'-azobis-2,4-dimethylvaleronitrile, 2,2'-azobismethylisobutylate and the like. Among them, 2,2'-azobismethylisobutylate is
20 preferably used from a viewpoint that a high molecular weight of water-soluble copolymer having alkyl-modified carboxyl groups can be obtained.

[0023]

25 The amount of the polymerization initiator to be used is desirably 0.00003-0.002 moles with respect to 1 mole of (meth)acrylic acid. When the amount of the polymerization

initiator is less than 0.00003 moles, it is possible that the polymerization reaction rate is slow and not economical. When the amount of the polymerization initiator is more than 0.002 moles, it is possible that the polymerization progresses rapidly to make reaction control difficult.

[0024]

The reaction temperature is preferably 50-90 °C, more preferably 55-75 °C. When the reaction temperature is lower than 50 °C, it is possible that the viscosity of the reaction solution increases to make uniform-stirring difficult. When the reaction temperature is above 90 °C, it is possible that the polymerization progresses rapidly to make reaction control difficult.

The reaction time, which depends on the reaction temperature, is usually 0.5-5 hours.

[0025]

The water-soluble copolymer having alkyl-modified carboxyl groups of the present invention may be obtained by heating the reaction solution for example at 80-130 °C after completion of the reaction to evaporate the solvent. When the heating temperature is lower than 80 °C, it is possible that it takes long time to evaporate the solvent. When the heating temperature is above 130 °C, it is possible that water-solubility of the obtained water-soluble copolymer having alkyl-modified carboxyl groups deteriorates.

[0026]

The water-soluble copolymer having alkyl-modified carboxyl groups thus obtained is characterized in that a 1 weight %-neutralized viscous liquid obtained from the copolymer shows a viscosity of 1000 mPa·s or lower and a transmittance of 95 % or higher, and when 1-7 parts by weight of sodium chloride is added to 100 parts by weight of the neutralized viscous liquid, the liquid shows a highest viscosity of 10000-30000 mPa·s and a transmittance of 95 % or higher. Usually, a liquid is considered to be significantly transparent when a transmittance is 95 % or higher.

[0027]

In viscosity measurements, 1 weight %-neutralized viscous liquids having with a pH of 6.5-7.5, which is formed by dissolving a predetermined amount of the water-soluble copolymers to an appropriate amount of pure water with stirring and adding a predetermined concentration of sodium hydroxide or, if required, electrolyte-added solutions prepared by adding a predetermined amount of sodium chloride and stirring are used as evaluation samples after standing for one hour.

Viscosity is measured at 25 °C after one minute rotating at a rotational speed of 20 rpm by using a BH type rotational viscometer with a spindle rotor No. 6.

[0028]

In the present invention, a transmittance is measured at a wavelength of 425 nm in a cell with a light path length of 1 cm after degassing a sample by centrifuging.

[0029]

5 For example, neutralized viscous liquids which have a pH of 6.5-7.5 and contain the water-soluble copolymer having alkyl-modified carboxyl groups according to the present invention at about 1 weight % may be used as a thickening agent for cosmetics and the like, wherein the
10 neutralized viscous liquids are formed by dissolving the copolymer to pure water such as deionized water and neutralizing with alkali.

Alkalis used to neutralize the copolymer solution are not particularly limited but include alkali metal
15 hydroxides such as sodium hydroxide, amines such as triethanolamine, diisopropanolamine, and the like. Among them, sodium hydroxide is preferably used.

[0030]

The neutralized viscous liquids obtained from the
20 water-soluble copolymer having alkyl-modified carboxyl groups according to the present invention have a very low viscosity when no electrolyte exists and have a greatly increased viscosity when electrolytes are added. Further, the neutralized viscous liquids have a sufficiently high
25 viscosity and a very high transmittance and have moist textures without stickiness even in the presence of a

relatively high concentration of electrolytes.

[0031]

It is not clearly understood why the water-soluble copolymer having alkyl-modified carboxyl groups according to the present invention shows the above property. However, it is presumed that by using a specific amount of lauryl (meth)acrylate, the lauryl groups introduced into the water-soluble copolymer having alkyl-modified carboxyl groups associate with each other in an aqueous solution via hydrophobic interaction to increase viscosity and thereby effects of electrolytes change.

[0032]

Accordingly, use of the water-soluble copolymer having alkyl-modified carboxyl groups according to the present invention allows for the manufacture of cosmetics with excellent transparency and having moist texture without stickiness regardless of a relatively high concentration of various electrolytes as additives.

Such cosmetics include, for example, lotion, emulsion, serum, cream, cream pack, massage cream, cleansing cream, cleansing gel, cleansing foam, sunscreen, styling gel, eyeliner, mascara, lipstick, foundation and the like.

[0033]

In addition, due to a low viscosity in the absence of electrolytes, those thickening agents are very useful from a viewpoint of manufacturing efficiency for cosmetics and

the like. That is, since a viscosity of a solution may be maintained to low in a variety of manufacturing processes before adding electrolytes, working efficiencies in a reaction process, a transfer process, a heating process, a compounding process and the like before adding electrolytes may be greatly improved by allowing for a process to add electrolytes later.

Effect of the Invention

10 [0034]

The present invention provides a water-soluble copolymer having alkyl-modified carboxyl groups which is able to produce a neutralized viscous liquid in which although its viscosity is very low when no electrolyte exists, the viscosity greatly increases when electrolytes are added, which has a sufficiently high viscosity and which has a very high transmittance and moist textures without stickiness even in the presence of a relatively high concentration of electrolytes.

20

Best mode for carrying out the Invention

[0035]

The present invention will be specifically explained below by referring to the following Examples, Comparative Examples and Reference Examples. However, the present invention is never limited by those examples.

[0036]

Example 1

Into a 500 mL-four necked flask equipped with a stirrer, a thermometer, a nitrogen blowing tube and a condenser, were placed 45 g (0.625 moles) of acrylic acid; 2.7 g of lauryl methacrylate; 150 g of normal hexane and 0.081 g (0.00035 moles) of 2,2'-azobismethylisobutylate. The mixture was stirred and mixed uniformly followed by blowing a nitrogen gas into the solution in order to remove oxygen existing in the upper portion of the reactor vessel, the raw materials and the solvent. Then, a reaction was conducted for 4 hours at 60-65 °C under a nitrogen atmosphere. After the reaction was completed, the formed slurry was heated at 90 °C to evaporate normal hexane and, further, the resultant product was dried under reduced pressure at 10 mmHg at 110 °C for 8 hours to obtain 45 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0037]

Example 2

The manner in Example 1 was followed but the amount of lauryl methacrylate was changed to 4.1 g to obtain 46 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0038]

Example 3

The method of Example 1 was followed but 0.02 g of pentaerythritol allyl ether was added in addition to 45 g (0.625 moles) of acrylic acid, 2.7 g of lauryl methacrylate, 150 g of normal hexane and 0.081 g (0.00035 moles) of 2,2'-azobismethylisobutylate to obtain 45 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0039]

Example 4

The method of Example 3 was followed but the amount of lauryl methacrylate was changed to 4.1 g to obtain 46 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0040]

Comparative Example 1

The method of Example 1 was followed but the amount of lauryl methacrylate was changed to 1.8 g to obtain 44 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0041]

Comparative Example 2

The method of Example 1 was followed but the amount of lauryl methacrylate was changed to 5.4 g to obtain 47 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0042]

Comparative Example 3

The method of Example 3 was followed but the amount of pentaerythritol allyl ether was changed to 0.13 g to obtain 45 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0043]

Comparative Example 4

The method of Example 3 was followed but 4.1 g of stearyl methacrylate was used in place of 2.7 g of lauryl methacrylate to obtain 47 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0044]

Comparative Example 5

The method of Example 3 was followed but 0.9 of stearyl methacrylate was used in place of 2.7 g of lauryl methacrylate and the amount of pentaerythritol allyl ether was changed to 0.09 g from 0.02 g to obtain 44 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0045]

Main raw materials and their amounts used in Examples 1-4 and Comparative Examples 1-5 are summarized in Tables 1 and 2.

[0046]

Table 1

Main raw material	Ex. 1	Ex. 2	Ex. 3	Ex. 4
acrylic acid [g]	45 (100)	45 (100)	45 (100)	45 (100)
lauryl methacrylate [g]	2.7 (6)	4.1 (9.1)	2.7 (6)	4.1 (9.1)
pentaerythritol allyl ether [g]	-	-	0.02 (0.044)	0.02 (0.044)

The number in a parenthesis indicates an amount of the respective raw materials in parts by weight with assuming the amount of the acrylic acid used as 100 parts by weight.

[0047]

Table 2

Main raw material	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
acrylic acid [g]	45 (100)	45 (100)	45 (100)	45 (100)	45 (100)
lauryl methacrylate [g]	1.8 (4)	5.4 (12)	2.7 (6)	-	-
stearyl methacrylate [g]	-	-	-	4.1 (9.1)	0.9 (2)
pentaerythritol allyl ether [g]	-	-	0.13 (0.29)	0.02 (0.044)	0.09 (0.2)

The number in a parenthesis indicates an amount of the respective raw materials in parts by weight with assuming the amount of the acrylic acid used as 100 parts by weight.

[0048]

Evaluations

- In order to evaluate properties as a thickening agent of water-soluble copolymers having alkyl-modified carboxyl groups obtained in Examples 1-4 and Comparative Example 1-5, viscosity and transmittance measurements were carried out

regarding 1 weight %-neutralized viscous liquids of
respective copolymers and electrolyte-added solutions
prepared by adding sodium chloride to the liquids and
mixing. Further, among these electrolyte-added solutions,
5 those showing the highest viscosity were subjected to a
moisture sensory test.

[0049]

(1) Preparation of evaluation samples

Three grams of each of the water-soluble copolymers
10 having alkyl-modified carboxyl groups obtained in Example
1-4 and Comparative Examples 1-5 was gradually added and
dissolved to 280 g of pure water (deionized water) with
stirring. To the solution was added 17 g of 6 weight %-
sodium hydroxide to form 1 weight %-neutralized viscous
15 liquids with a pH of 6.5-7.5. In addition, 1-7 weight %-
electrolyte-added solutions were prepared by adding 3 g, 6
g, 9 g, 12 g, 15 g, 18 g, or 21 g of sodium chloride to 300
g of 1 weight %-neutralized viscous liquids obtained
according to the manner as the same as above in order to
20 evaluate properties of these neutralized viscous liquids in
the presence of electrolytes.

[0050]

In the following evaluations, these 1 weight %-
neutralized viscous liquids and the various weight %-
25 electrolyte-added solutions were used as evaluation samples
after standing for one hour.

[0051]

(2) Viscosity measurement

With respect to each of the evaluation samples, viscosity was measured at 25 °C after one minute rotating at a rotational speed of 20 rpm by using a BH type rotational viscometer with a spindle rotor No. 6. Measurement results are shown in Tables 3-7.

[0052]

(3) Transmittance measurement

With respect to each of the evaluation samples, transmittance was measured at a wavelength of 425 nm in a cell with a light path length of 1 cm after degassing by centrifuging at 2000 rpm for 30 minutes. Usually, a liquid is considered to be very transparent by visual observation when transmittance is 95 % or higher. Measurement results are shown in Tables 3-7.

[0053]

(4) Sensory Evaluation on Texture

Respective evaluation samples which exhibited the highest viscosity in viscosity measurements with respect to each of the water-soluble copolymers having alkyl-modified carboxyl groups obtained in Examples 1-4 and Comparative Examples 1-5 were applied on skins of panelists consisting of 5 men and 5 women. Texture was evaluated based on feeling when the sample was spread with fingers.

Evaluation criteria are as follows:

A: moisture

B: relatively moisture

C: no impression

D: sticky

5 [0054]

Additionally, when 70 % or more of the panelists score "A: moisture" or "B: relatively moisture" to a sample, the sample is considered to show moisture texture. The evaluation results are shown in Tables 8-9.

10 [0055]

Table 3

Amount of NaCl added [g]	Ex. 1			Ex. 2		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	110	99		250	99	
3	4310	98		25000	97	Sample for S.E.
6	17000	97		14250	96	
9	18700	98	Sample for S.E.	7100	95	
12	14100	96		4000	94	
15	9700	96		2250	92	
18	5500	94		1800	91	
21	1600	92		1500	90	

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0056]

Table 4

Amount of NaCl added [g]	Ex. 3			Ex. 4		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	240	99		300	99	
3	2940	98		26500	98	Sample for S.E.
6	16750	98		15000	97	
9	19300	96	Sample for S.E.	6900	92	
12	15000	95		4500	94	
15	10450	94		2000	91	
18	7650	92		1900	91	
21	3760	90		1200	90	

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0057]

Table 5

Amount of NaCl added [g]	Comp. Ex. 1			Comp. Ex. 2		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	188	99		340	97	
3	44	98		18550	84	Sample for S.E.
6	106	98		4340	57	
9	776	96		2900	34	
12	2990	95		800	8	
15	4800	94		--	--	phase sep.
18	8000	92	Sample for S.E.	--	--	phase sep.
21	7250	90		--	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0058]

Table 6

Amount of NaCl added [g]	Comp. Ex. 3			Comp. Ex. 4		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	5700	96		15200	97	Sample for S.E.
3	7100	88	Sample for S.E.	6800	56	
6	4900	65		250	14	
9	2200	13		--	--	phase sep.
12	50	2		--	--	phase sep.
15	--	--	phase sep.	--	--	phase sep.
18	--	--	phase sep.	--	--	phase sep.
21	--	--	phase sep.	--	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0059]

Table 7

Amount of NaCl added [g]	Comp. Ex. 5		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	6800	95	
3	9550	87	Sample for S.E.
6	6150	63	
9	1700	13	
12	400	4	
15	--	--	phase sep.
18	--	--	phase sep.
21	--	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0060]

Table 8

Criteria	Ex. 1 [people]	Ex. 2 [people]	Ex. 3 [people]	Ex. 4 [people]
A	9	0	7	1
B	1	8	2	7
C	0	2	1	2
D	0	0	0	0

[0061]

Table 9

Criteria	Comp. Ex. 1 [people]	Comp. Ex. 2 [people]	Comp. Ex. 3 [people]	Comp. Ex. 4 [people]	Comp. Ex. 5 [people]
A	8	8	8	1	7
B	2	1	1	0	2
C	0	1	1	1	1
D	0	0	0	8	0

[0062]

From Tables 3-9, it is understood that the water-soluble copolymers having alkyl-modified carboxyl groups obtained in Examples 1-4 produced a neutralized viscous liquid in which although its viscosity is very low when no electrolyte exists, the viscosity greatly increases when electrolytes are added, which has a sufficiently high viscosity and a very high transmittance and which has moist textures without stickiness even in the presence of a relatively high concentration of electrolytes.

[0063]

Thus, it is demonstrated that the water-soluble copolymers having alkyl-modified carboxyl groups obtained in Examples 1-4 can be used as a thickening agent having excellent properties as described above.

[0064]

Reference Example 1

Components 1-6 shown below were added at the respective percentages and uniformly mixed by stirring.

5 Further, components 7-10 were added and uniformly mixed by stirring and solbilized to prepare lotion.

	1. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 4)	0.1%
10	2. Sodium hydroxide	0.28%
	3. 2-glucoside ascorbate	2.0%
	4. Citric acid	0.01%
	5. Sodium hydrogenphosphate	0.1%
	6. Distilled water	balance to 100 % sum
15	7. Ethanol	8.0%
	8. POE(30) POP(6) decyl tetradecyl ether	0.3%
	9. Preservative	q.s.
	10. Incense	q.s.

* q.s.: quantum sufficiat

20 [0065]

Reference Example 2

Components 1-8 shown below were added at the respective percentages and heated at 80 °C. Further, components 9-17 were added and heated at 80 °C followed by stirring to emulsify. Then, emulsion was prepared by cooling with stirring.

25

	1. POE(20) sorbitan monostearate	1.0%
	2. POE(40) sorbitol tetraoleate	1.5%
	3. Lipophilic glyceryl monostearate	1.0%
5	4. Stearic acid	0.5%
	5. Behenyl alcohol	1.5%
	6. Squalane	5.0%
	7. Cetyl 2-ethylhexanoate	5.0%
	8. Methyl polysiloxane	0.5%
10	9. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 2)	0.1%
	10. Xanthan gum	0.1%
	11. Sodium hydroxide	0.05%
	12. Sodium lactate	1.0%
15	13. Citric acid	0.01%
	14. Sodium hydrogenphosphate	0.1%
	15. 1,3-butylene glycol	7.0%
	16. Preservative	q.s.
	17. Distilled water	balance to 100 % sum

20 * q.s.: quantum sufficiat

[0066]

Reference Example 3

Components 1-11 shown below were added at the respective percentages and dissolved at room temperature to form a viscous liquid. Then, serum was prepared.

1. Water-soluble copolymer having alkyl-modified carboxyl

	groups (Example 1)	0.2%
	2. Sodium hydroxide	0.08%
	3. L-ascorbyl magnesium phosphate	3.0%
	4. Sodium Citrate	0.5%
5	5. Tetrasodium EDTA	0.1%
	6. 1,3-butylene glycol	7.0%
	7. Glycerin	8.0%
	8. Distilled water	balance to 100 % sum
	9. Cosmetic component	q.s.
10	10. Preservative	q.s.
	11. Ethanol	5.0%

* q.s.: quantum sufficiat

[0067]

Reference Example 4

15 Components 1-6 shown below were added at the
 respective percentages and heated at 80 °C. Further,
 components 7-14 were added at the respective percentages,
 heated at 80 °C, and stirred to emulsify. Then, cream was
 prepared by cooling with stirring.

20

	1. Decaglyceryl pentaoleate	3.0%
	2. Beeswax	2.0%
	3. Cetanol	2.0%
	4. Squalane	5.0%
25	5. Glyceryl tri-2-ethylhexanoate	2.0%
	6. Methyl polysiloxane	0.5%

	7. Glycerin	5.0%
	8. L-ascorbyl magnesium phosphate	3.0%
	9. Sodium citrate	0.5%
	10. Tetrasodium EDTA	0.1%
5	11. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 3)	0.15%
	12. Sodium hydroxide	0.06%
	13. Preservative	q.s.
	14. Distilled water	balance to 100 % sum
10	* q.s.: quantum sufficiat	

[0068]

Reference Example 5

Components 1-4 shown below were added at the respective percentages and heated at 80 °C. Further, components 5-12 were added at the respective percentages, heated at 80 °C, and stirred to emulsify. Then, cream pack was prepared by cooling with stirring.

	1. POE(20) POP(4) cetyl ether	0.8%
20	2. Diglyceryl monostearate	0.2%
	3. Glyceryl tri-2-ethylhexanoate	1.0%
	4. Meduhome oil	1.0%
	5. Glycerin	5.0%
	6. 1,3-butylene glycol	3.0%
25	7. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 2)	0.1%

	8. Sodium hydroxide	0.28%
	9. Hydroxyethyl cellulose	0.3%
	10. 2-Glucoside ascorbate	2.0%
	11. Preservative	q.s.
5	12. Distilled water	balance to 100 % sum

* q.s.: quantum sufficiat

[0069]

Reference Example 6

Components 1-7 shown below were added at the respective percentages and heated at 80 °C. Further, components 8-13 were added at the respective percentages, heated at 80 °C, and stirred to emulsify. Then, massage cream was prepared by cooling with stirring.

15	1. POE(20) cetyl ether	2.0%
	2. Lipophilic glyceryl monostearate	4.0%
	3. Cetanol	2.0%
	4. White vaseline	6.0%
	5. Squalane	30.0%
20	6. Glyceryl tri-2-ethylhexanoate	5.0%
	7. Methyl polysiloxane	0.5%
	8. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 4)	0.1%
	9. Sodium hydroxide	0.04%
25	10. Glycerin	5.0%
	11. Sodium PCA	1.0%

12. Preservative q.s.

13. Distilled water balance to 100 % sum

* q.s.: quantum sufficiat

[0070]

5 Reference Example 7

Components 1-7 shown below were added at the respective percentages and heated at 80 °C. Further, components 8-13 were added at the respective percentages, heated at 80 °C, stirred to emulsify. Then, cleansing
10 cream was prepared by cooling with stirring.

	1. POE(20) sorbitan monostearate	2.0%
	2. POE(40) sorbitol tetraoleate	1.0%
	3. Self-emulsifying glyceryl monostearate	2.0%
15	4. Stearic acid	4.0%
	5. Cetanol	2.0%
	6. Liquid paraffin	30.0%
	7. Glyceryl tri-2-ethylhexanoate	10.0%
	8. 1,3-butylene glycol	5.0%
20	9. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 2)	0.1%
	10. Sodium hydroxide	0.04%
	11. L-serine	1.0%
	12. Preservative	q.s.
25	13. Distilled water	balance to 100 % sum

* q.s.: quantum sufficiat

[0071]

Reference Example 8

Components 1-10 shown below were added at the respective percentages and uniformly mixed at room temperature to form gel. Then, cleansing gel was prepared.

	1. AQUPEC HV-501E™ (carboxyvinyl polymer)	0.1%
	2. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 1)	0.1%
10	3. Sodium hydroxide	0.08%
	4. Sodium PCA	1.0%
	5. Hydroxypropyl cellulose	0.5%
	6. POE(30) cetyl ether	16.0%
	7. POE(5) lauryl ether	12.0%
15	8. 1,3-butylene glycol	10.0%
	9. Distilled water	balance to 100 % sum
	10. Preservative	q.s.

* q.s.: quantum sufficiat

[0072]

20 Reference Example 9

Components 1-8 shown below were added at the respective percentages and heated at 80 °C. Further, components 9-14 were added at the respective percentages, heated at 80 °C and mixed. Then, cleansing foam was prepared by cooling with stirring.

	1. Myristic acid	15.0%
	2. Palmitic acid	5.0%
	3. Stearic acid	3.0%
	4. Beeswax	3.0%
5	5. Polyethylene glycol 6000	2.0%
	6. Ethylene glycol distearate	2.0%
	7. Diethanolamide cocoate	3.0%
	8. Concentrated glycerin	15.0%
	9. Water-soluble copolymer having alkyl-modified carboxyl	
10	groups (Example 3)	0.1%
	10. Sodium hydroxide	0.04%
	11. Potassium hydroxide	5.5%
	12. Sodium PCA	0.5%
	13. Sodium N-lauroylsarcosine	10.0%
15	14. Distilled Water	balance to 100 % sum
	[0073]	

Reference Example 10

Components 1-10 shown below were added at the respective percentages and heated at 80 °C. Further, components 11-16 were added at the respective percentages, heated at 80 °C and stirred to emulsify. Then, sunscreen was prepared by cooling with stirring.

25	1. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 4)	0.1%
	2. Sodium carboxymethylcellulose	0.3%

	3. Sodium hydroxide	0.28%
	4. 2-glucoside ascorbate	2.0%
	5. Citric acid	0.01%
	6. Sodium hydrogenphosphate	0.1%
5	7. Preservative	q.s.
	8. 1,3-butylene glycol	7.0%
	9. Glycerin	8.0%
	10. Distilled water	balance to 100 % sum
	11. Sorbitan monostearate	0.5%
10	12. Polyoxyethylene sorbitan POE(20) monooleate	0.5%
	13. Sorbitan sesquioleate	0.5%
	14. Cetanol	2.0%
	15. 2-ethylhexyl paramethoxycinnamate	10.0%
	16. Ethanol	10.0%
15	* q.s.: quantum sufficiat	

[0074]

Reference Example 11

Components 1-6 shown below were added at the respective percentages and dissolved at room temperature. Then, styling gel was prepared by stirring to uniformly mix.

	1. AQUPEC HV-505E (carboxyvinyl polymer)	0.1%
	2. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 3)	0.1%
25	3. Sodium hydroxide	0.08%
	4. Vinylpyrrolidone-vinyl acetate copolymer solution (H)	

(*1)	10.0%
5. Sodium PCA	1.0%
6. Distilled water	balance to 100 % sum

*1: PVP/VAE-735 manufactured by ISP Corporation

5 [0075]

Reference Example 12

Components 1-9 shown below were added at the respective percentages and dissolved at room temperature. Then, eyeliner was prepared by stirring to uniformly mix.

10

1. Alkyl acrylate copolymer emulsion (*2)	30.0%
2. 1,3-butylene glycol	15.0%
3. Black iron oxide	15.0%
4. Water-soluble copolymer having alkyl-modified carboxyl	
15 groups (Example 1)	0.1%
5. Sodium hydroxide	0.04%
6. Sodium carboxymethylcellulose	2.0%
7. Sodium chloride	0.5%
8. Preservative	q.s.
20 9. Distilled water	balance to 100 % sum

* q.s.: quantum sufficiat

*2: YODOSOL GH810™ manufactured by Nippon NSC Ltd.

[0076]

Reference Example 13

25

Components 1-10 shown below were added at the respective percentages and heated at 80 °C. Further,

components 11-16 were added at the respective percentages, heated at 80 °C and stirred to emulsify. Then, mascara was prepared by cooling with stirring.

5	1. Stearic acid	2.0%
	2. Carnauba wax	2.0%
	3. Beeswax	3.0%
	4. Polyoxyethylene sorbitan POE(20) monooleate	1.0%
	5. Sorbitan sesquioleate	0.5%
10	6. Alkyl acrylate copolymer emulsion (*2)	1.0%
	7. Triethanolamine	1.1%
	8. Propylene glycol	1.0%
	9. Black iron oxide	10.0%
	10. Kaolin	10.0%
15	11. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 1)	0.2%
	12. Sodium hydroxide	0.08%
	13. Sodium carboxymethylcellulose	2.5%
	14. Sodium chloride	0.1%
20	15. Preservative	q.s.
	16. Distilled water	balance to 100 % sum

* q.s.: quantum sufficiat

*2: YODOSOL GH810 manufactured by Nippon NSC Ltd.

[0077]

25 Reference Example 14

Components 1-11 shown below were added at the

respective percentages and dispersed by roll milling. The resultant product was poured into a mold at a high temperature. Then, lipstick was prepared by filling the cooled and molded product into a container.

5

	1. Candelilla wax	5.0%
	2. Ceresin	5.0%
	3. Carnauba wax	3.0%
	4. Microcrystalline wax	3.0%
10	5. Glyceryl tri-2-ethylhexanoate	20.0%
	6. Isotridecyl isononanoate	20.0%
	7. Diisostearyl maleate	balance to 100 % sum
	8. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 4)	1.0%
15	9. Silicic anhydride	1.0%
	10. Coloring agent	q.s.
	11. Preservative	q.s.

* q.s.: quantum sufficiat

[0078]

20 Reference Example 15

Components 1-11 shown below were added at the respective percentages and heated at 80 °C. Further, components 12-17 were added at the respective percentages, heated at 80 °C and mixed. Then, foundation was prepared by cooling with stirring.

25

	1. Lipophilic glyceryl monostearate	1.0%
	2. Stearic acid	5.0%
	3. Behenyl alcohol	1.0%
	4. Cetanol	0.5%
5	5. Squalane	5.0%
	6. Titanium oxide	4.0%
	7. Red iron oxide	q.s.
	8. Yellow iron oxide	q.s.
	9. Black iron oxide	q.s.
10	10. Talc	4.0%
	11. Soy bean phospholipid	0.3%
	12. 1,3-butylene glycol	8.0%
	13. Triethanolamine	1.5%
	14. Water-soluble copolymer having alkyl-modified carboxyl	
15	groups. (Example 4)	0.2%
	15. Sodium hydroxide	0.08%
	16. Sodium PCA	1.0%
	17. Distilled water	balance to 100 % sum

* q.s.: quantum sufficiat

20 [0079]

The cosmetics which use the water-soluble copolymer having alkyl-modified carboxyl groups obtained in Examples 1-4 showed moisture texture without stickiness. In addition, cosmetics and the like containing electrolytes and the like showed similar properties.

25

What we claimed is:

1. A water-soluble copolymer having alkyl-modified carboxyl groups which is obtained by polymerizing 100 parts by weight of (meth)acrylic acid, 5-10 parts by weight of lauryl (meth)acrylate, and 0.001-0.044 parts by weight of a compound having two or more ethylenic unsaturated groups, wherein a 1 weight %-neutralized viscous liquid shows a viscosity of 1000 mPa·s or lower and a transmittance of 95 % or higher, and when 1-7 parts by weight of sodium chloride is added to 100 parts by weight of the neutralized viscous liquid, the liquid shows a highest viscosity of 10000-30000 mPa·s and a transmittance of 95 % or higher, wherein the 1 weight %-neutralized viscous liquid is a liquid containing 1 weight % of said water-soluble copolymer having alkyl-modified carboxyl groups which has been neutralized with an alkali.

2. The water-soluble copolymer having alkyl-modified carboxyl groups according to claim 1, wherein the compound having two or more of ethylenic unsaturated groups is at least one selected from a group consisting of pentaerythritol allyl ether, diethylene glycol diallyl ether, polyethylene glycol diallyl ether and polyallyl saccharose.

3. A thickening agent comprising the water-soluble copolymer having alkyl-modified carboxyl groups according to claim 1 or 2.