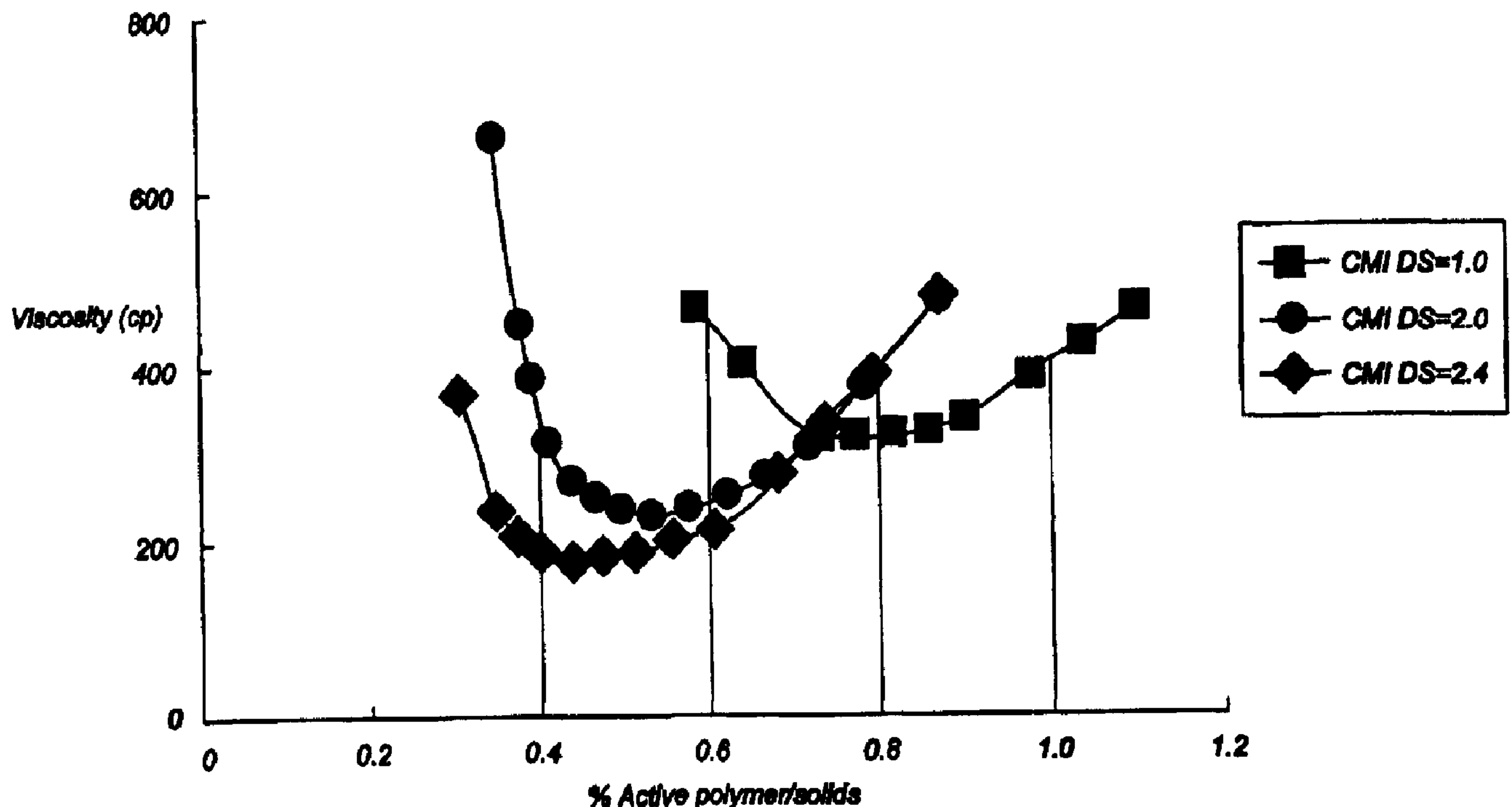




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(54) Title: FRUCTAN DERIVATIVES AS DISPERSING AGENTS



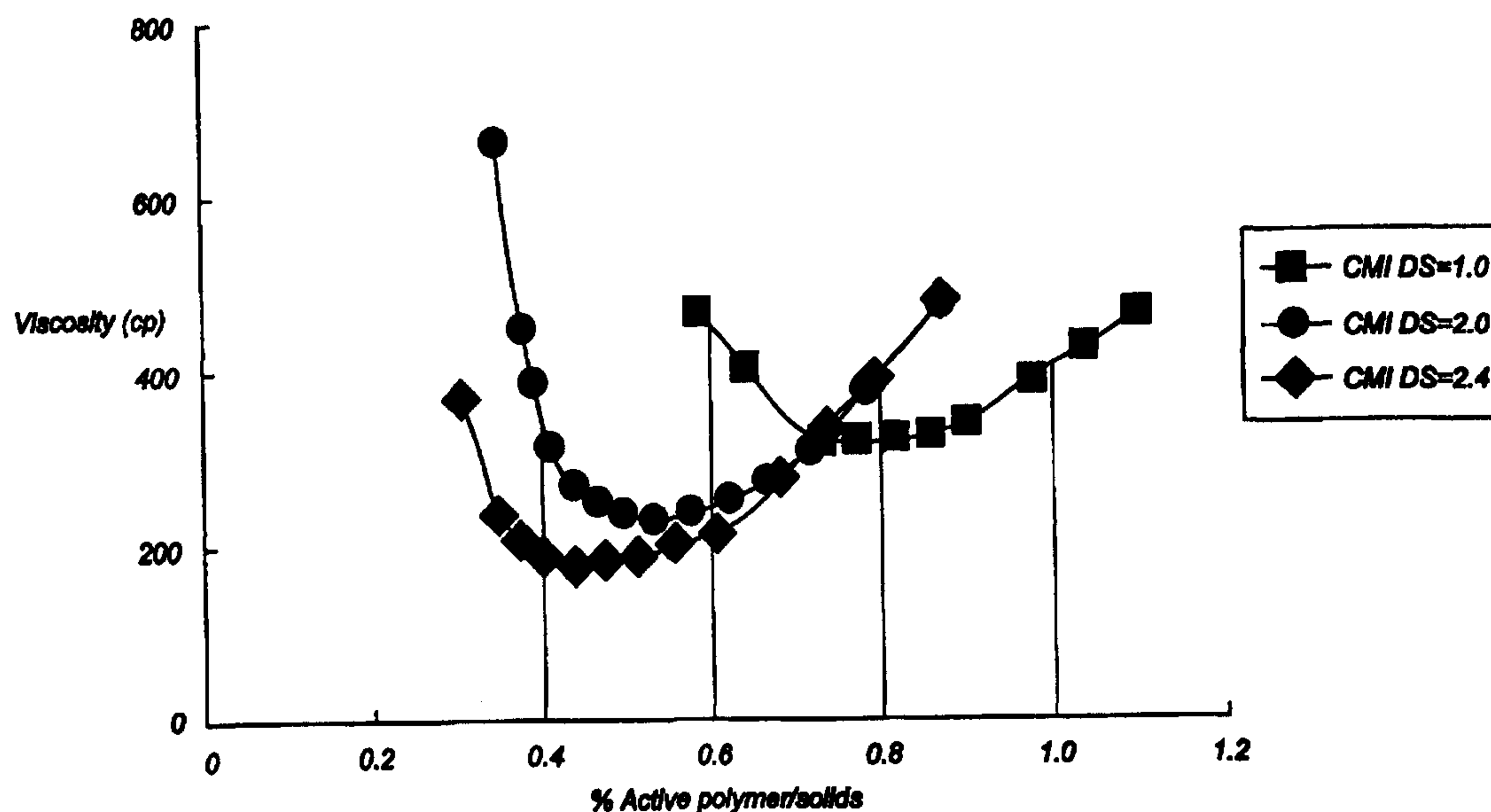
(57) Abrégé/Abstract:

Dispersions of pigment, such as calcium carbonate, titanium dioxide and types of clay, can be effectively stabilised by the use of a carboxyl-containing fructan in an amount of 0.05 - 10 % by weight, based on the dispersion, which fructan contains 0.5 - 3 carboxyl groups per mono-saccharide unit. The carboxyalkyl groups are in particular carboxymethyl groups, but the carboxyl groups can also be carboxyl groups obtained entirely or partially by oxidation. The carboxymethylfructan gives results which are comparable to or better than those obtained with the polyacrylates which are less desirable from the standpoint of health and environment.

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(21) International Application Number: PCT/NL99/00359 (22) International Filing Date: 9 June 1999 (09.06.99) (30) Priority Data: 1009379 11 June 1998 (11.06.98) NL (71) Applicant (for all designated States except US): COÖPERATIE COSUN U.A. [NL/NL]; Oostelijke Havendijk 15, P.O. Box 1308, NL-4700 BH Roosendaal (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): KUZEE, Hendrika, Cor- nelia [NL/NL]; Bermweg 51, NL-4388 CB Oost-Souburg (NL). RAAIJMAKERS, Hendricus, Wilhelmus, Carolina [NL/NL]; Hoveniersberg 33, NL-4708 HD Roosendaal (NL). (74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibu- reau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>

(54) Title: DISPERSING AGENT**(57) Abstract**

Dispersions of pigment, such as calcium carbonate, titanium dioxide and types of clay, can be effectively stabilised by the use of a carboxyl-containing fructan in an amount of 0.05 – 10 % by weight, based on the dispersion, which fructan contains 0.5 – 3 carboxyl groups per mono-saccharide unit. The carboxyalkyl groups are in particular carboxymethyl groups, but the carboxyl groups can also be carboxyl groups obtained entirely or partially by oxidation. The carboxymethylfructan gives results which are comparable to or better than those obtained with the polyacrylates which are less desirable from the standpoint of health and environment.

Fructan Derivatives as Dispersing Agents

The invention relates to the use of specific fructan derivatives as a dispersing agent.

Dispersed solid particles usually have the tendency to flocculate and/or to precipitate. A
5 dispersing agent prevents this flocculation and as a result stabilises the dispersion. In addition, a
dispersing agent lowers the viscosity of the dispersion. As a result the dispersions can be pumped
or processed more easily at higher concentrations of solid particles. This is important both from the
technical and from the economic standpoint.

Phosphates and polyphosphates, such as sodium hexametaphosphate, are widely used as
10 inorganic dispersing agents. These inorganic agents have a good dispersing action but have the
disadvantage that they are not stable to hydrolysis. As a result, the viscosity of the dispersion will
increase in the course of time.

Organic dispersing agents used are polymers and copolymers of acrylic acid and
methacrylic acid having a molecular weight of 5,000 to 100,000. For instance, dispersions of more
15 than 50 % by weight of solid particles (such as clay particles) with a polyacrylate as dispersing
agent are described in WO 95/25146. DE-A 2 700 444 describes the use of copolymers of maleic
acid, JP-A-56-115630 that of unsaturated sulphonic acids and EP-A 705 893 that of
phosphonocarboxylic acids as dispersing agents or as deflocculants.

The disadvantage of the organic dispersing agents used to date is that they are all based on
20 petrochemical, and thus non-renewable, raw materials. Furthermore, these substances are poorly
degradable and/or toxic to surface water or soil. There is therefore a need for organic dispersing
agents which score better than the known petrochemical products with regard to these aspects.

It has been found that carboxyl-containing fructans and salts thereof meet this need. These
derivatives have a dispersing action for solid substances, in particular pigments, are biodegradable
25 and are non-toxic. The invention therefore relates to a method for the preparation of dispersions
and to dispersions obtainable in this way, as described in the appended claims.

In this context fructans are understood to include all oligosaccharides and polysaccharides
which have a majority of anhydrofructose units. The fructans can have a polydisperse chain length
distribution and can be straight-chain or branched. The fructan can contain mainly β -2,6 bonds, as

in levan. Preferably the fructan contains mainly β -2,1 bonds, as in inulin.

In this context carboxyl-containing fructans are understood to be a derivative of inulin or another fructan that contains 0.3-3 carboxyl groups per anhydrofructose unit. In particular the derivative contains at least 0.8 carboxyl groups per anhydrofructose unit. The carboxyl groups can be present in the form of carboxyalkyl groups, such as carboxymethyl, carboxyethyl, dicarboxymethyl or carboxyethoxycarbonyl groups. These can be obtained by etherification of the fructan in a known manner. Preferably, the carboxyl-containing fructan contains 0.7-2.5 carboxymethyl groups per monosaccharide unit. The carboxyl groups can also be present in the form of oxidised hydroxymethylene or hydroxymethyl groups. Mixed carboxyfructans can also be used. Preferably, the number of carboxymethyl groups is greater than the number of other carboxyl groups. Carboxymethylinulin (CMI) is the most preferred.

Carboxymethylinulin (CMI) with a DS (degree of substitution) of 0.15-2.5 is disclosed in WO 95/15984 and in the article by Verraest et al. in *JAOCs*, 73 (1996) pp. 55-62. It is prepared by reaction of a concentrated solution of inulin with sodium chloroacetate at elevated temperature. Carboxylethylinulin (CEI) is disclosed in WO 96/34017. The oxidation of inulin is, for example, disclosed in WO 91/17189 and WO 95/12619 (C3-C4 oxidation, leading to dicarboxylinulin, DCI) and WO 95/07303 (C6 oxidation). In the case of mixed carboxyl derivatives the inulin can have been first carboxymethylated and then oxidised or (preferably) the other way round.

The carboxyl-containing fructan has an average chain length (= degree of polymerisation, DP) of at least 3, rising to about 1000. Preferably, the average chain length is 6-60 monosaccharide units. The fructan can optionally have been subjected to a reduction treatment beforehand in order to remove reducing groups.

Modified fructan derivatives which according to the invention can be converted to carboxyalkylfructan are, for example, fructans in which the chain length has been enzymatically extended, and fructan hydrolysis products, that is to say fructan derivatives having a shortened chain, and fractionated products having a modified chain length. Fractionation of fructans such as inulin can be effected by, for example, low temperature crystallisation (see WO 94/01849), column chromatography (see WO 94/12541), membrane filtration (see EP-A 440 074 and EP-A 627 490) or selective precipitation with alcohol. Prior hydrolysis to produce shorter fructans can, for example, be effected enzymatically (endo-inulinase), chemically (water and acid) or by

heterogeneous catalysis (acid column). Hydroxyalkylated and/or cross-linked fructans also come into consideration for use in the method according to the invention after carboxyalkylation and, if appropriate, oxidation.

5 The carboxymethylfructan can be used in the form of the purified substance, but use can also be made of the technical grade product obtained directly by carboxymethylation. Specifically, it has been found that any impurities, such as glycolic acid and diglycolic acid, have no adverse effects on the action of the CMI. It is possible to make use of the free acid, but also of a salt, such as the sodium, potassium or ammonium salts.

10 The solid to be dispersed or suspended can be any solid which is sufficiently chemically inert to be able to be dispersed or suspended in water. The particles are usually inorganic and insoluble in water. Examples are talc, barite, calcium carbonate, mica, kaolin, bentonite and other types of clay, zinc oxide, calcium sulphate, zeolite, carbon, haematite and the like. The carboxyfructans can be used as dispersing agents for soluble or semi-soluble solids.

15 Dispersions of calcium carbonate and titanium dioxide can be used in paints and other coating compositions. Other widely used pigments which can be dispersed using the carboxyfructans according to the invention are, for example, iron oxide, carbon black and aluminium stearate. The pigment can also be a corrosion-inhibiting pigment, such as red lead, zinc oxide, zinc powder or aluminium powder, citrates and the like. It is also possible to prepare bentonite dispersions, which can be used as softeners in, for example, detergents and weighting
20 materials in drilling muds. Furthermore, the carboxyfructans can be used for a wide variety of dispersions of low viscosity, for coating paper. Pigments which can be used for this purpose are, for example, kaolin, satin white, calcium carbonate and talc. Other uses are e.g. in dispersing mining products.

For rapid dispersion the particle size of the solids is preferably as small as possible,
25 preferably less than 1 mm and in particular between 1 and 50 μm . The solids concentration is 1 - 90 % by wt based on the total weight of the dispersion. From the economic standpoint, the concentration is at least 30 % by wt rising to, for example, 80 % by wt.

The carboxyl-containing fructan can first be mixed with the pigment (or other substance to be dispersed or to be suspended) and then added to the water, or it can first be added to the water
30 before the pigment is added with vigorous stirring.

The quantity of carboxyl-containing fructan, in particular CMI, is in general between 0.05 and 10 % by wt, in particular between 0.2 and 2 % by wt, based on the solid to be dispersed. The dispersion can contain 0.002-5%, preferably 0.015-3% by weight of carboxyl-containing fructan based on the total weight of the dispersion. It is also possible to use mixtures of the carboxyl-
 5 containing fructan and other dispersing agents, such as polyacrylates or phosphonates, preferably in a ratio of at least 1 part carboxyl-containing fructan to one part other agent. The pH of the dispersion system is usually neutral to slightly alkaline (pH 6 - 12); the pH is often above 7. If necessary, other solvents, such as alcohols, can be added to the water; however water usually suffices.

10 The carboxyl-containing fructans have a dispersing action, expressed in number of mols carboxyl groups that is required per tonne dry pigment (see WO 97/10308), which is as good as or even better than that of polyacrylates.

EXAMPLES

15 Example 1

CMI with a DS (degree of substitution; average number of substituents per monosaccharide unit) of 2.4 and 100 % DCI were compared with a commercial polyacrylate (PA, mol. wt. 4500) that is used for dispersing calcium carbonate in the paints industry. An initial dosage of dispersing agent was added to 250 g CaCO₃ (Socal P2, Solvay) in 150 g water. Small dosages of dispersing solution
 20 were then added to the dispersion. The concentration of the dispersing solutions was 1 % solids. After each addition the viscosity of the dispersion was measured at 25 °C using a Brookfield viscometer. The results are given in Table 1.

Table 1

% Dispersing agent with respect to pigment	Viscosity (Pas)		
	CMI	DCI	PA (comp.)
0	16.3	16.3	16.3
0.05	14.2	11.2	16.5
0.075	12.2	9.3	16.6

0.10	8.8	7.1	11.2
0.125	5.5	4.7	5.2
0.15	2.9	3.2	4.2

Example 2

The viscosity of the following paint formulation (parts by weight) was determined 1 day and 28 days after making up and storing at 50 °C.

5

	water	274.5
	Tylose (trade-mark) MH 30000 yp2	3
	NaOH 10 %	1
	Calgon (trade-mark) N 10 %	5
10	Tiona (trade-mark) RCL-535	30
	Socal (trade-mark) P2	120
	Omyacarb (trade-mark) 2 GU	120
	Omyacarb (trade-mark) 5 GU	280
	industrial lacker	100
15	Mowilith (trade-mark) LDM 1871	60
	Mergal (trade-mark) K9N	2
	Byl (trade-mark) 033	2
	Dispersing agent 30 % in water	2.5

20 The results are as follows:

Dispersing agent	Viscosity (mPas)	
	After 1 day	After 28 days
Polyacrylate A (comparative)	5000	4600
Polyacrylate B (comparative)	5500	5700
CMI DS 1.5	6100	7600
CMI DS 2.4	4800	4600
DCI 60 %	600	5700
DCI 100 %	5500	5700

Example 3

Various CMI products were compared with a commercial polyacrylate in the dispersion of calcium

sulphoaluminate of the formula $3\text{CaOAl}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. The concentration of the slurry was 50 %. It was investigated how much dispersing agent at 30 °C is needed to reduce the viscosity of the slurry to 25 mPas (Brookfield viscometer 60 rpm). It can be seen from the results given below that compared with the polyacrylate in particular the CMI products with a relatively low DS require
 5 fewer carboxyl groups to lower the viscosity to the set value.

Dispersing agent	Consumption % based on wet slurry	Carboxyl groups % based on wet slurry
CMI DS 0.5	0.94	0.16
CMI DS 1.0	0.82	0.23
CMI DS 1.5	0.83	0.30
CMI DS 2.5	0.90	0.42
Polyacrylate A (comp.)	0.44	0.31

Example 4

Effect of the carboxyl content of CMI on dispersion of kaolin.

10 An initial dosage of dispersing agent was added to 269.4 g kaolin in 115.5 g water. Small dosages of dispersing solution were then added to the dispersion. The concentration of the dispersing solutions was 40 % solids. After each addition the viscosity of the dispersion was measured at 25 °C using a Brookfield viscometer. The results are given in the appended figure.

Claims

1. A method for preparing a stable dispersion of solids in an aqueous medium using a polycarboxy compound, characterised in that a carboxymethylinulin that contains 0.3 to 3 carboxyl groups per monosaccharide unit is incorporated in the medium and/or in the solids, and the solids concentration in the stable dispersion is between 1 and 90 weight %.
2. The method according to Claim 1, wherein 0.05 to 10 % by weight of the carboxymethylinulin is used, based on the solid to be dispersed.
3. The method according to Claim 1 or 2, wherein the carboxymethylinulin contains at least 0.8 carboxyl group per monosaccharide unit.
4. The method according to one of Claims 1 to 3, wherein the carboxymethylinulin contains 0.7 to 2.5 carboxymethyl groups per mono-saccharide unit.
5. The method according to one of Claims 1 to 4, wherein the carboxymethylinulin has an average degree of polymerisation of 6 to 60.
6. The method according to one of Claims 1 to 5, wherein the solid to be dispersed is a pigment or a type of clay.
7. The method according to one of Claims 1 to 6, wherein a product obtained directly by carboxymethylation of inulin is used.
8. The method according to one of Claims 1 to 6, wherein a purified carboxy-methyl-inulin is used.
9. A stable dispersion of a pigment in an aqueous medium, which contains 1 to 90 % by weight of the pigment and 0.002 to 5 % by weight of a carboxymethylinulin that contains 0.3 to 3 carboxyl groups per monosaccharide unit, the percentages by weight being based on the total weight of the dispersion.
10. The stable dispersion according to Claim 9, which contains 30 to 80 % by weight of the pigment and 0.015 to 3 % by weight of the carboxymethylinulin, based on the dispersion.

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