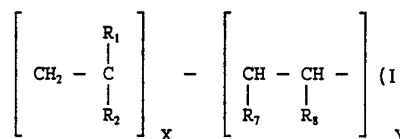
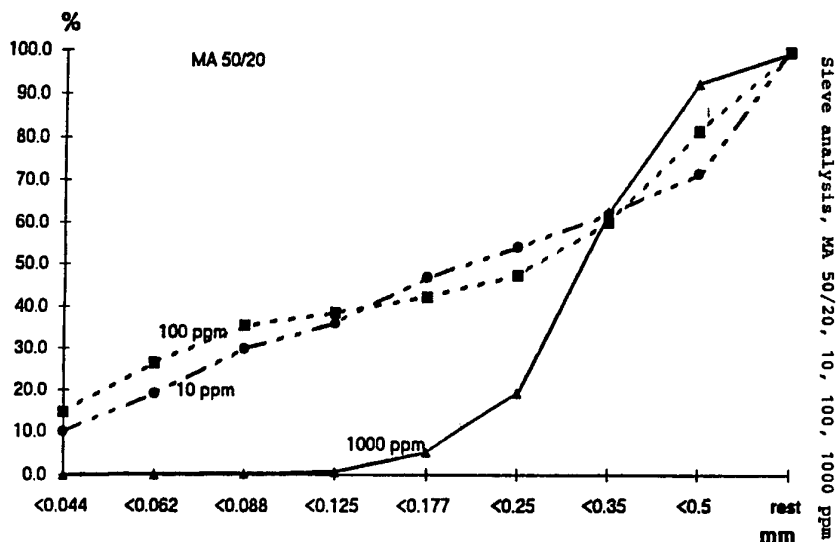




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(54) Title: A PROCESS FOR PREPARING A CRYSTALLINE, STABLE SODIUM PERCARBONATE



(57) Abstract

The object of the invention is a process for preparing a crystalline, stable sodium percarbonate, in which polymers of gross formulas (I or II) are added in the preparation process to control the crystal form of the sodium percarbonate and to coat the crystals, the molecular weight of the polymers varying in the range from 500 to 1 000 000 g/mol, or salts of these polymers or mixtures of polymers of formulas (I and II) or of their salts are added. Formula (I) denotes (I) and formula (II) denotes (II): HO-(-CH₂-CH₂-O)_r-(CHCH₃-CH₂-O)_s-(-CH₂-CH₂-O)_t-H and X < 100 % and Y > 0 %, R₁ is -H or -CH₃, R₂ is -COOM, in which M may be H⁺ or a cation, in particular Na⁺, K⁺ or NH₄⁺, R₇ and R₈ may be identical or different, being -COOM, -CONR₅R₆, H, -OH or -COO(-CH₂-CH₂-O)_r-(CHCH₃-CH₂-O)_s-(-CH₂-CH₂-O)_t-H and R₅ and R₆ are -H or an alkyl group, in particular C₁-C₄ and may be mutually identical or different groups and r, t and s may vary respectively in the range from 0 to 100 %, their sum being 100 %.

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A process for preparing a crystalline, stable sodium percarbonate

The invention relates to a process for preparing a crystalline, stable sodium percarbonate by crystallizing an aqueous solution of starting materials.

Sodium percarbonate is a water-soluble, crystalline peroxygen compound with the molecular formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$. It has a theoretical active oxygen concentration (AO) of 15.28% by weight. Sodium percarbonate is relatively well water-soluble, sodium carbonate and hydrogen peroxide being released in the solution. Owing to this characteristic sodium percarbonate has, in fact, a widespread application as a bleaching agent. It is particularly suitable for bleaching textiles and for removing coloured stains from textiles in industry and households.

Compared to another common bleaching agent, sodium perborate, sodium percarbonate is considerably faster dissolved in cold water and does not require any special bleaching activator, and is thus also energy-saving. Moreover, compared to perborates and chlorous bleaching agents, sodium percarbonate does not generate any polluting residues.

The stocking of sodium percarbonate involves certain problems. In a cooled, dry storage it is conserved as such for long periods of time. If, however during storage, the relative humidity of air is greater than the critical relative humidity of the product sodium percarbonate will absorb water from the surrounding air. This process is enhanced by a temperature raise and causes a reduction of the AO concentration as a function of time. Sodium percarbonate will be dissolved in the absorbed water into a saturated solution consisting of sodium carbonate and hydrogen peroxide. Sodium carbonate increases the basicity of the

solution, which, again, accelerates the natural decomposition of hydrogen peroxide in the solution. Moreover, due to the preparation process and the raw materials, impurities may occur in the product, which accelerate the decomposition of hydrogen peroxide. Such impurities with a catalytic activity are transition metal ions, among others.

In fact, when preparing sodium percarbonate with crystallization methods, it is commonly known to carry out a preliminary purification of sodium carbonate by adding water-soluble Mg salt to its solution, the Mg salt precipitating magnesium carbonate from the solution and metal salt impurities being coprecipitated. In addition to this, the product may be stabilized by adding agents complexing the metal salts concerned and by precipitating finely-divided magnesium silicate in the product, which will protect the hydrogen peroxide in the product against heterogenic decomposition by catalysis of the surfaces of solid impurities.

Because of the catalytic decomposition mechanism, the water absorption tendency of the product can be reduced in the preparation step, since thus the amount of solution phase formed by absorbed water and sodium percarbonate in the finished product, in which dissolved hydrogen peroxide is apt to be decomposed, will be small.

Certain requirements are posed on the physical properties of the product crystals depending on the way the product is used. Thus, the crystals should not generate dust, and also, their size and the bulk density of the product formed by them should be appropriate to be admixed with other detergent components and also adequate for normal packing techniques. These additional requirements have resulted in the practical need to use additives controlling crystal growth in the preparation step, called "crystal modifiers", in order to obtain the desired physical properties of the crystals.

Several methods using crystal modifiers for preparing sodium percarbonate to be used as a bleaching agent are previously known. One way of increasing the stability of sodium percarbonate is to use aminopolycarboxyl acid and/or α -hydroxyacrylic acid as modifiers in the crystallization, as described in the patent specifications JP 63 147 804, JP 63 215 502 and JP 1153 510 (Nippon Peroxide).

DE 2 364 634 (Degussa) discloses a process for preparing sodium percarbonate, in which polycarboxylates are added to the reaction mixture of alkali carbonate and hydrogen peroxide. Besides acrylic acid or its derivative, polycarboxylates contain vinyl alcohol derivatives and acrolein.

According to DE published patent application 23 03 627 (ICI) a water-soluble polyelectrolyte is used as a means for salting out sodium percarbonate crystals. Acrylic polymers are mentioned as appropriate polyelectrolytes.

GB patent specification 1469 352 (Peroxid-Chemie) describes a process for preparing sodium percarbonate by adding hexametaphosphate or polyacrylate as a modifier to the sodium carbonate solution.

Though there have been attempts to enhance the chemical properties and the suitability as a detergent component of sodium percarbonate with several processes, commercially available sodium percarbonate products are still extremely instable and their crystal size is not suitable to be used in detergent powders.

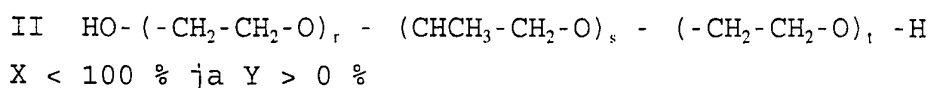
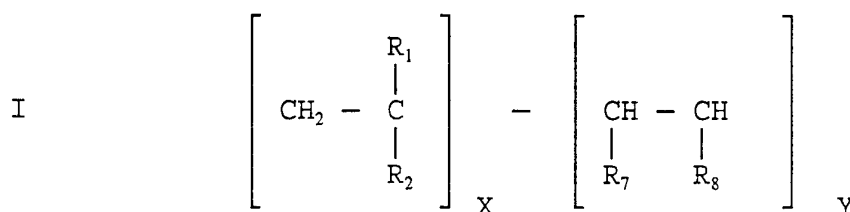
The purpose of this invention is to provide a process that enables to yield sodium percarbonates having a good mechanical strength, an adequate particle size and a good ability to conserve active oxygen.

The object mentioned above is achieved by using organic polymers according to the invention to control the crystal form of sodium percarbonate and to coat the crystals.

Sodium percarbonate crystals that were surprisingly stable and only slightly hygroscopic were obtained by using the polymers of claim 1 as crystal modifiers. The crystals were confirmed to have a regular rounded shape and the crystal size (0.1 to 1 mm) was particularly suitable to be used along with other detergent components. Only a reduced amount of material having too fine a crystal size or an inadequate shape was produced. The average bulk density of the product was in the range from 0.5 to 0.6 g/cm³ and the active oxygen concentration was approx. 14%.

The sodium percarbonate crystals preserved their active oxygen concentration for quite a long time. Only 0.9 to 1.5% of the active oxygen had disappeared during a stocking of six weeks, at a temperature of 30°C and in a relative humidity of 70%. Tests in similar conditions for hygroscopicity yielded equally good results.

The process according to the invention uses organic polymers for controlling the crystal form of sodium percarbonate and for coating the crystals, the polymers having a molecular weight in the range of 500 to 1 000 000 g/mol and the following molecular formula



R_1 is -H or -CH₃

R_2 is -COOM, in which M may be H⁺ or a cation, especially Na⁺, K⁺ or NH₄⁺

R_7 and R_8 may be identical or different, being -COOM, -CONR₅R₆, H, -OH or

-COO(-CH₂-CH₂-O)_r - (CHCH₃-CH₂-O)_s - (-CH₂-CH₂-O)_t - H and

in which R₅ and R₆ are -H or alkyl groups, especially C₁-C₄ and may be identical or different groups and r, t and s may vary respectively in the range from 0 to 100%, their sum being 100%. Copolymers defined in formulas (I) and (II) may be random, alternating or block copolymers.

The polymers of formula I and II are known per se.

Appropriate polymers are methacrylic, acrylic and maleic or fumaric acid copolymers and/or their salts or (meth)acrylic acid and acrylamide copolymers and/or their salts or ethylene oxide and propylene oxide copolymers or mixtures of these polymers. Copolymers of acrylic acid and maleic acid, their salts, copolymers of acrylic acid and acrylamide, their salts, copolymers of ethylene oxide and propylene oxide, and mixtures of all the above polymers are cited as particularly appropriate polymers.

In terms of the invention, sodium percarbonate was prepared by adding simultaneously a soda solution and an aqueous solution of hydrogen peroxide into a simulated mother liquor. Metal impurities were removed from the soda solution by means of magnesium sulfate before the use. Sodium silicate had been added to the aqueous solution of hydrogen peroxide in order to stabilize the solution. The mother liquor contained a soda solution, a polymer for modifying and coating the crystals, as well as sodium chloride for salting out. Sodium percarbonate crystals were added to the mother liquor as seed crystals at the stage when the mother liquor became slightly turbid. The reaction temperature was 20°C and the mixing rate

142 rpm. The sodium percarbonate crystals formed were washed with an aqueous solution of soda and hydrogen peroxide and were dried over night.

The appropriate polymer concentration varies in the range from 10 to 1000 ppm, being preferably about 100 ppm. The polymer concentration denotes the concentration of formula I or II or mixtures of them or the concentration of the salts of such polymers or polymer mixtures.

The polymers appropriate for modifying and coating the crystals allow wide variations of the preparation process. As the polymer concentration increases the crystallization rate decreases, whereas the bulk density and the crystal size grow. Also, as the polymer concentration increases, the "coarseness" of the crystals disappears. (Figures 1 and 2). The polymer concentration did not apparently affect the decomposition rate of sodium percarbonate. On the other hand, sodium chloride used for salting out does affect the decomposition rate. When sodium chloride was not used at all, the decomposition rate of the sodium percarbonate crystals was approx. 2.5 times as rapid. When the hydrogen peroxide solution was first added to the mother liquor, needle-shaped crystals inadequate for the purpose were obtained.

Appropriate polymers have a molecular weight in the range from 1000 to 200 000 g/mol, in particular from 2000 to 130 000 g/mol.

A number of embodiment examples are presented below with the only purpose to illustrate the present invention.

Example 1

Sodium percarbonate was prepared as follows:

127 g of 50% aqueous solution of hydrogen peroxide and 375 g of 30% aqueous solution of Na_2CO_3 were simultaneously added to a mother liquor containing 7.5 g of Na_2CO_3 , 55 g of NaCl , 200

g of water and 10 to 1000 ppm of organic polymer (tables 1 and 2), for one hour at room temperature and by stirring at a rate of 142 rpm. The aqueous solution of hydrogen peroxide had been stabilized with an aqueous solution of sodium silicate (1.84 g of sodium silicate had been dissolved in 5 g of water).

The aqueous solution of sodium carbonate had been purified with magnesium sulfate.

After the hydrogen peroxide solution and the soda solution had been added, the mother liquor was stirred for half an hour more. Sodium percarbonate seed crystals were added to the mother liquor as the solution started to become opaque.

The crystals were filtered, washed with an aqueous solution of sodium percarbonate, which had been obtained by dissolving 22.5 g of $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$ in 150 g of water. The crystals were dried at a temperature of 30°C over night.

Table 1.

Organic polymers used for controlling the crystal shape of sodium percarbonate

Polymer		Maleic acid ^x	Acrylic acid ^x	Molecular weight
		%	%	g/mol
Fennodispo B41	1)	80	20	3000-4000
MA 50/70	2)	50	50	70000
MA 50/20	2)	50	50	20000
MA 30/130	2)	30	70	130000
MA 30/40	2)	30	70	40000
Sokalan CP12S	3)	30	70	3000
Fennodispo A47	4)			4000

1) a maleic acid and acrylic acid copolymer, in which an ethylene oxide and propylene oxide copolymer has been grafted on to one of the carboxylic groups of maleic acid (Kemira)

2) sodium salt of maleic acid and acrylic acid copolymer (Kemira)

3) sodium salt of maleic acid and acrylic acid copolymer (Sokalan Basf)

4) sodium salt of acrylic acid and acrylamide copolymer (Kemira)

x maleic acid and acrylic acid concentrations without side chains. (Except for Fennodispo B41, for which the figures of the table indicate the ratio between maleic acid and acrylic acid).

Table 2.

The effect of the polymer concentration used for controlling the crystal form

Polymer	ppm ¹	Active oxygen concn. %	Bulk density g/cm ³	Yield ² %	<0.35 mm %	<0.25 mm %
MA 50/20	10	13.6	0.48	71.8	62.1	54.1
MA 50/20	100	13.5	0.51	70.0	60.2	47.5
MA 50/20	1000	14.4	0.90	32.0	62.7	19.3

1) dry-matter content of the polymer calculated on the total amount of reactants used for the crystallization

2) the yield percentage has been calculated after a settling of two hours

The results in table 2 lead to the conclusion that as the polymer concentration grows from 10 to 1000 ppm the crystallization rate decreases (the yield is reduced), whereas the bulk density and the crystal size grow.

Example 2.

Table 3 illustrates the active oxygen concentration (AO), bulk density, crystal size distribution, decomposition and hygroscopicity of stable sodium percarbonate.

Table 3.

100 ppm of polymer was used for controlling the crystal form.

Polymer	AO ¹⁾ %	Bulk densit y g/cm ³	Yield ²⁾ %	Crystal size <0.35%	Decom- position % (rel.) t=611h ³⁾	Pick up of moisture % t=611 h ³⁾
Fenno- dispo B41	14.1	0.59	58.0	92.8	4.3	2.4
MA 50/70	13.6	0.56	63.3	61.3	3.8	1.0
MA 50/20	13.5	0.51	70.0	60.2	8.0	0.2
MA 30/130	13.9	0.53	66.0	65.2	5.2	2.8
MA 30/40	14.4	0.58	66.6	49.4	5.6	2.6
Sok.CP12S	14.4	0.76	69.3	31.6	3.6*	2.1*

*t=641 h

1) active oxygen concentration

2) calculated yield % = $100 \times (\text{Na}_2\text{CO}_3 \times 1.5 \text{ H}_2\text{O}_2) \text{ molecular quantity} / \text{Na}_2\text{CO}_3 \text{ molecular quantity}$

3) at a temperature of 30°C and a 70% relative humidity, in open dishes throughout all stability tests

When polymers of the MA range are being used, 50 to 65% of the sodium percarbonate crystals obtained are under 0.35 mm. When Sokalan CP12S polymer are used, "coarser" crystals are obtained (32% are under 0.35 mm). Fennodispo B41 polymer yields more finely-divided crystals than the polymers of the MA range (93% are under 0.35 mm). The bulk density varies from 0.51 to 0.58 g/cm³ for the polymers of the MA range, for Sokalan CP12S 0.76 g/cm³ was yielded and for Fennodispo B41 the outcome was 0.59 g/cm³.

Stability tests

Table 4.

Active oxygen concentration and decomposition

Temperature 30°C, relative humidity 70%, 100 ppm of polymer

Polymer	Active oxygen (%)					Decomposition (%) per week			
	0 h	164	448	611	990	164h	448	611	990
Ferro-dispo B41	13.8	13.6	13.5	13.2	12.8	1.48	0.82	1.20	1.23
MA 50/70	13.0	13.0	12.7	12.5	12.0	0.00	0.87	1.06	1.31
MA 50/20	13.8	13.3	12.8	12.7	12.3	3.71	2.72	2.19	1.87
MA 30/130	13.5	13.0	12.8	12.8	12.5	3.79	1.94	1.43	1.26
MA 30/40	14.2	13.8	13.6	13.4	13.1	2.89	1.58	1.55	1.31
Sokl.CP12S	14.0	13.7	13.7*	13.5*		2.20	1.10 **	0.94 **	

*t= 326 h and t= 641 h

**t = 326 h and t= 641 h

Table 5.

Hygroscopicity tests

Temperature 30°C, relative humidity 70%, 100 ppm of polymer

Polymer	Pick up of moisture, H ₂ O %				
	Time h	0 h	164	448	611
Fennodispo B41	0	1.8	2.0	2.4	3.6
MA 50/70	0	0.6	0.9	1.0	2.3
MA 50/20	0	0.6	0.2	0.2	1.2
MA 30/130	0	2.7	2.7	2.8	3.9
MA 30/40	0	1.4	2.0	2.6	3.8
Sokl.CP12S	0	1.2	2.0*	2.1*	

* t= 326 h and t=641 h

The AO concentration decreased by 0.3 to 0.6% during the first week when using the polymers of the MA range (30°C, relative humidity 70%). At the end of six weeks the AO concentration was 0.9 to 1.5% lower. When using Fennodispo MA 50/70 polymer there was no decrease at all in the first week.

The average decomposition per week was 1 to 2% in a test series of six weeks. The decomposition rate was clearly higher in the first week than in the subsequent weeks.

Example 3.

The decomposition and moisture content of sodium percarbonate crystals prepared according to the invention were compared to a commercially available sodium percarbonate product prepared by Interox. The tests were performed at a temperature of 40°C and a 75% relative humidity.

Table 6.

Decomposition and hygroscopicity tests
 Temperature 40°C, relative humidity 75%

Polymer	Decomposition (%) per week	Pick up of moisture (%) per week
Interox*	46	39
Fenno- dispo A47	8	8
Fenno- dispo B41	7	2
MA50/70	4	2

* compared to a commercially available sodium percarbonate product

With regard to the outcome it can be noted that the products according to the invention were decomposed considerably slower and their pick up of moisture content was markedly lower than that of the commercially available product.

Example 4

In continuous, experimental preparation of sodium percarbonate 20 kg/h of 50% H₂O₂, which also contained 0.45% MgCl₂, was fed into a vacuum crystallizer of MSMPR type with a 200 l liquid volume, and additionally 100 kg/h of soda solution, which had been precleaned with MgCl₂. The concentration of the soda solution was 20% Na₂CO₃, 10% NaCl and 0.12% Na₂SiO₃. Moreover, Fennodispo B41 was added into the crystallizer as a crystal modifier in an amount such as to form a concentration in the crystallizer representing a) 10 ppm and b) 100 ppm. A 30°C temperature and a 45 mbar absolute pressure were maintained in the crystallizer, the average residence time being 2 h. The crystal slurry containing 17.5% of SPC(sodium percarbonate) crystals was removed from the

crystallizer continuously about 100 l/h, the crystals were separated from the mother liquor with a vacuum band filter and washed with a water solution saturated with regard to SPC. The water content of the washed humid crystal cake was 19% in test a) and respectively 18% in test b).

The analysis results of the samples dried in a fluidized-bed drier are presented in table 7.

Table 7. Fluidized-bed dried SPC samples of a continuous Pilot scale crystallizer with Fennodispo B41 as a crystal modifier a) 10 pp, b) 100 ppm

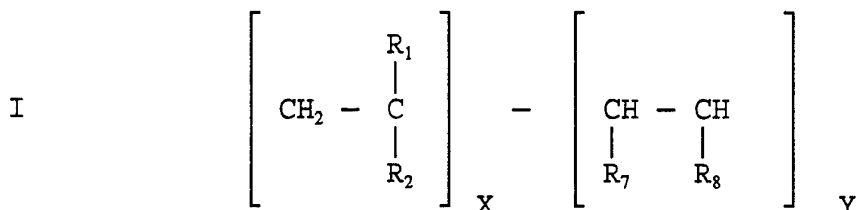
Process step	a	b
AO, %	15.2	15.2
SPC (calculated on AO) %	99.4	99.2
Cl, %	0.1	0.1
H ₂ O, %	0.1	0.2
Bulk density, g/cm ³	0.85	0.85
Decomposition per week, %	*) 2.1	0.52
Moisture absorption per week, %	*) 0.01	0.00

*) Calculated on the outcome of a stability test of one week. Testing conditions: 30°C and 70% (RH = relative humidity).

The test indicates that a good product quality is maintained or even improved, particularly with regard to hygroscopicity, when the process of the invention is implemented in continuous production.

Claims

1. A process for preparing a crystalline, stable sodium percarbonate, **characterized** in that for controlling the crystal form of the sodium percarbonate and for coating the crystals, polymers of gross formula I or II are added into the preparation process, their molecular weight varying in the range from 500 to 1 000 000 g/mol, or salts of these polymers or mixtures of the polymers of formulas I and II or of their salts, formula I denoting:



and formula II denoting



in which $X < 100\%$ and $Y > 0\%$

R_1 is $-\text{H}$ or $-\text{CH}_3$

R_2 is $-\text{COOM}$, in which M may be H^+ or a cation, in particular Na^+ , K^+ or NH_4^+

R_7 , R_8 may be identical or different, being $-\text{COOM}$, $-\text{CONR}_5\text{R}_6$, H , $-\text{OH}$

or $-\text{COO}(-\text{CH}_2 - \text{CH}_2 - \text{O})_r - (\text{CHCH}_3 - \text{CH}_2 - \text{O})_s - (-\text{CH}_2 - \text{CH}_2 - \text{O})_t - \text{H}$ and R_5 and R_6 are $-\text{H}$ or an alkyl group, in particular $\text{C}_1 - \text{C}_4$, being mutually identical or different groups, and in which r , t and s may vary respectively in the range from 0 to 100%, their sum being 100%.

2. A process according to claim 1, **characterized** in that a polymer is used for controlling the crystal form of the sodium percarbonate and for coating the crystals, the polymer being a methacrylic or acrylic acid copolymer with maleic acid or a sodium, potassium or ammonium salt of such a copolymer.

3. A process according to claim 1, **characterized** in that a polymer is used for controlling the crystal form of the sodium percarbonate and for coating the crystals, the polymer being a methacrylic acid and acrylic acid copolymer with acrylic amide or a sodium, potassium or ammonium salt of such a copolymer.

4. A process according to claim 1, **characterized** in that a polymer is used for controlling the crystal form of the sodium percarbonate and for coating the crystals, the polymer being an ethylene oxide and propylene oxide copolymer or a maleic acid and acrylic acid copolymer, in which ethylene oxide and propylene oxide copolymer has been grafted on to one of the carboxyl groups of a maleic acid repeating unit.

5. A process according to any of claims 1 to 4, **characterized** in that the polymers of gross formulas I or II or salts of these polymers or mixtures of the polymers of formulas I and II or of their salts are used in amounts such that their concentration will be in the range from 10 to 1000 ppm, preferably 100 ppm.

6. A process according to any of claims 1 to 5, **characterized** in that the molecular weight of the polymers of gross formula I or II is in the range from 1000 to 200 000 g/mol, preferably from 2000 to 130 000 g/mol.

FIG. 1 Sieve analysis, MA 50/20, 10, 100, 1000 ppm

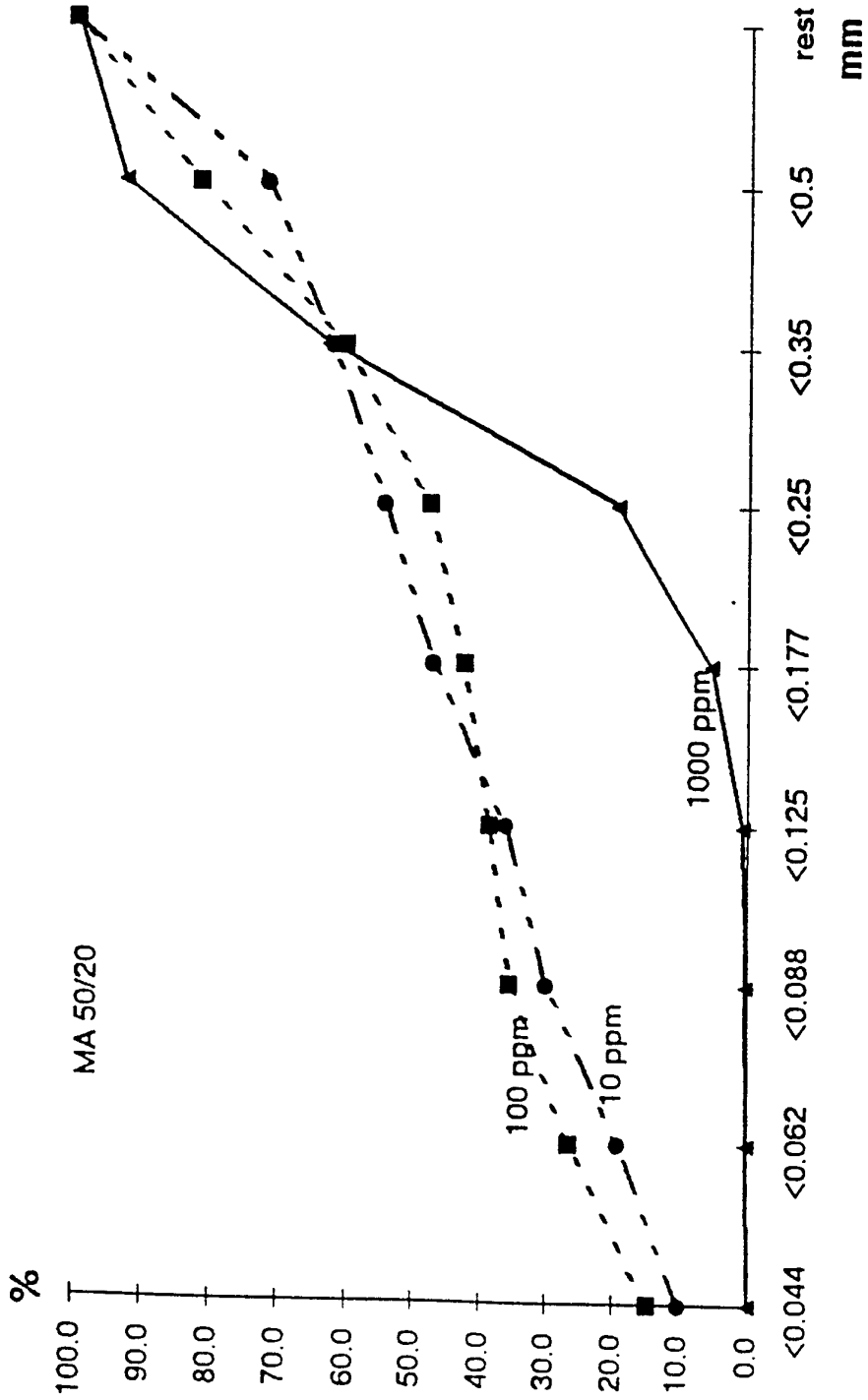
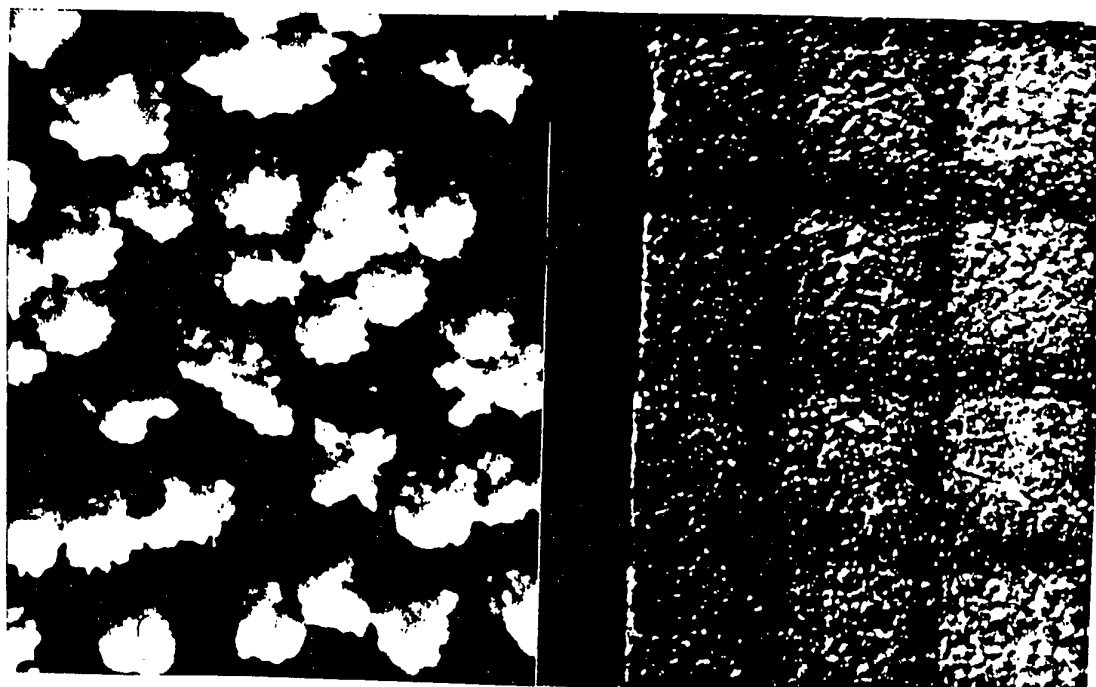


FIG. 2 Crystallization tests, MA 50/20, 10, 100, 1000 ppm

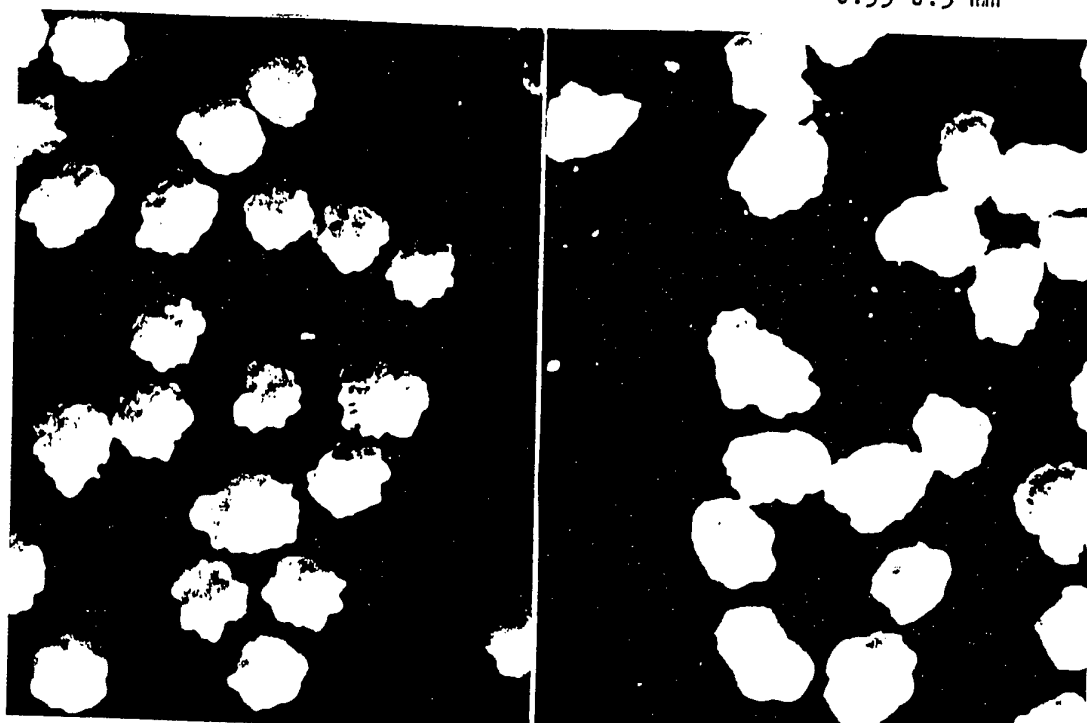


MA 50/20

10 ppm

crystal fraction

0.35-0.5 mm



MA 50/20

100 ppm

MA 50/20

1000 ppm

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 93/00356

A. CLASSIFICATION OF SUBJECT MATTER		
IPC5: C01B 15/10 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC5: C01B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE, B2, 2303627 (IMPERIAL CHEMICAL INDUSTRIES LTD.), 23 March 1978 (23.03.78), column 2, line 31 - line 50, claims 1-4 --	1-6
X	EP, A1, 0021498 (INTEROX SOCIETE ANONYME DITE), 7 January 1981 (07.01.81), page 2, line 33 - page 4, line 21, claims 1-5 -- -----	1
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search		Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT
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