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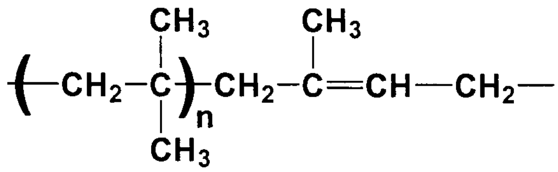
(54) **Title:** SUPERABSORBENT MATERIALS BASED ON BUTYL RUBBER PROCESS FOR MAKING SAID MATERIALS AND USE OF THEM

(57) **Abstract:** The invention relates to superabsorbent materials in the form of polymer membranes, rods or beads based on butyl rubber, which are hydrophobic, float on water and have a swelling capacity up to about 100 gram of organic solvent per gram of dry material. The invention also relates to solution and suspension crosslinking processes for the production of said superabsorbent materials and to the use of said superabsorbent materials for treatment of oil containing wastewater.

SUPERABSORBENT MATERIALS BASED ON BUTYL RUBBER PROCESS FOR MAKING SAID MATERIALS AND USE OF THEM

The present invention relates to superabsorbent materials in the form of polymer gels based on butyl rubber, to solution and suspension crosslinking processes for the production of said superabsorbent materials and to the use of said superabsorbent materials.

Butyl rubber, which is commercially available since 1943, consists of poly(isobutylene) chains containing small amounts (about 0.5 to 3 mol %) isoprene units. The structure of butyl rubber may be represented as follows, where n is a number between 30 to 200:



butyl rubber

Due to the low degree of unsaturation in butyl rubber, its vulcanization (crosslinking) requires much powerful accelerators than the natural rubber. Butyl rubber cannot be vulcanized with peroxides due to the chain scission reactions. For the preparation of heat resistant compounds, e.g., in cable insulation stocks, its vulcanization is carried out using dioximes. For exceptional heat resistant applications such as in tires, phenolic resins are used as the vulcanization agent. In general, butyl rubber can be vulcanized by three methods:

1) using elemental sulfur and an organic accelerator,
2) using polyfunctional nitroso compounds, and
3) using reactive methylolphenol resins.

Although a large number of patents and publications have been reported on the vulcanization of butyl rubber in bulk, no work has been found in the literature on its crosslinking in a solution.

Due to extensive chain scission reactions occurring in the presence of peroxide initiators such as dibenzoyl peroxide, solution crosslinking of butyl rubber by free-radicals cannot be carried out. The solution crosslinking of butyl rubber would lead to a pre-swollen crosslinked material. Such materials are called polymeric gels, which is a form of matter intermediate between a solid and a liquid. To understand the meaning of the term "gel", several definitions have been made. For example; P. H. Hermans in "Gels" Colloid Science, Vol.II, H.R. Kruyt (Ed), Elsevier Publishing Company, Inc., Amsterdam, page 483, (1949) "Gel is a system of at least two components. It exhibits mechanical properties characteristic of the solid state. The components of a gel extend continuously throughout the whole system", T. Tanaka in "Gels" Encyclopedia of Polymer Science and Engineering, Vol.7, A.Kingsberg & R. Piccininni (Eds), John Wiley & Sons, New York, USA, page 514 (1987) "Gel is a crosslinked polymer network swollen in a solvent", K. Almdal in K. Almdal, J. Dyre, J. Hvidt, O. Kramer, Polymer Gels and Networks, Vol. 1, page 5, Elsevier Science Publ., UK (1993) "A gel consists of two or more components, one of which is a liquid, present in substantial quantity. It is a soft, solid or solid-like material".

Polymeric gels consist of crosslinked long chain molecules immersed in a liquid medium. They play an important role in our lives and are nearly everywhere on earth. They are widely used for example as starting materials for ion-exchange resins, as absorbents in waste water treatment, as support carriers for immobilization of enzymes and cells in biotechnology and bioengineering as well as in the solid-state protein synthesis, as artificial organs, as catalysis in chemical engineering, as artificial snow, as artificial soils in agricultural engineering, etc.

The application field of polymeric gels expands as their properties are further improved. The synthesis of superabsorbent hydrophilic gels is an example for the recent developments in this field. All the Unites States, European and International patents on chemical and application aspects in superabsorbent polymeric gel production have recently been reviewed by Riccardo Po in the "Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics, Volume C34, pages 607- 662.

Although extensive works have been made in recent years on the synthesis of hydrophilic gels called hydrogels, little has been heard on their hydrophobic parents such as those based on butyl rubber. Moreover, preparation of polymeric gels based on butyl rubber by a solution crosslinking process has not been reported before.

Applicants have surprisingly found out that butyl rubber can easily be crosslinked in an organic solution using sulfur monochloride as a crosslinking agent and that, depending on the amounts of sulfur monochloride and butyl rubber in the crosslinking solution, hydrophobic gels with different swelling capacities can be synthesized.

The gels thus obtained can be used in a variety of applications such as in oil separating processes from aqueous solutions. For an economic oil extraction process, the gel must absorb large amounts of oil from aqueous solutions. Furthermore, the gel must be in the form of small particles for an effective oil separation - regeneration process and above all it should not sink in water. The present invention brings a solution to these problems.

The present invention relates to superabsorbent materials in the form of polymer gels based on butyl rubber. These materials are hydrophobic, float on water and have a swelling capacity up to about 100 g of organic solvent per gram of dry material and they are in the form of membranes, rods or beads. When they are in the form of mono-disperse, spherical gel beads they are in the size range of 0.1 to 2 mm in diameter.

The present invention relates also to suspension crosslinking process for the production of the above superabsorbent materials. In this process, a homogeneous solution of butyl rubber in an organic solvent is prepared under nitrogen atmosphere; Then sulfur monochloride is added into the polymer solution. This solution is added by stirring into an aqueous solution, optionally containing additives, to obtain an oil-in-water suspension. The discontinuous oil phase is crosslinked at constant stirring rate and spherical gel beads are obtained.

The present invention also relates to a solution crosslinking process for the production of superabsorbent materials. In this process, a homogeneous solution of butyl rubber in an organic solvent under nitrogen atmosphere is prepared. After addition of the crosslinking agent sulfur monochloride, polymer gels in the form of rods or membranes are obtained.

In these processes, the crosslinking is advantageously carried out at room temperature.

The butyl rubber concentration is with respect to the organic solvent at most 11w/v %, preferably between 3.5 and 10w/v %, especially 5w/v % and the sulfur monochloride concentration is with respect to butyl rubber between 0.6 and 80%, preferably between 0,6 and 5.0% and especially between 0,6 and 1.0. The stirring rate is at least 100 rpm, preferably between 200 and 700 rpm and especially 300 rpm.

The organic solvent used is a solvent with a solubility parameter close to that of butyl rubber, like chloroform, benzene, toluene, xylene, carbon tetrachloride and cyclohexane. The aqueous solution contains one or more additives chosen from the group consisting of a) sodium chloride, potassium chloride and b) alkaline earth phosphates, carbonates and silicates, starch, gelatin, poly (vinyl alcohol); poly (acrylic acid) and its salts; poly (vinyl pyrrolidone).

The present invention also relates to the use of the above superabsorbent materials for treatment of oil containing wastewater and to the use of the superabsorbent materials coming from a wastewater treatment as a fuel.

As stated before, the solution crosslinking of butyl rubber has not been described before. It has now been discovered that sulfur monochloride is an effective crosslinking agent for butyl rubber in organic solutions. The crosslinking agent sulfur monochloride, S_2Cl_2, is a liquid at room temperature and soluble in the organic solvents.

It has been found that "good solvents" for butyl rubber are suitable media for the solution crosslinking process. Since the solubility parameter δ of butyl rubber is 16.5 $(MPa)^{0.5}$, solvents with solubility parameters close to this value can be used in the crosslinking process. Examples are chloroform, benzene, toluene, xylene, carbon tetrachloride, and cyclohexane with δ = 18.9, 18.8, 18.2, 18.0, 17.6, and 16.8 $(MPa)^{0.5}$, respectively (C. M. Hansen, "Solubility Parameters", ASTM Manual 17, American Society for Testing and Materials, 1995).

Addition of a small quantity of sulfur monochloride into the organic solution of butyl rubber results in a pre-swollen gel at room temperature. Even at butyl rubber concentrations as low as 4w/v %, crosslinking reactions are complete at room temperature within a few hours. The crosslinking agent sulfur monochloride can be used at concentrations between 0.6 and 80 v/w % with respect to butyl rubber.

The present invention is explained more specifically in the following examples given merely for illustration purposes and making reference to the following figures, wherein:

Figure 1 represents the weight swelling ratio of butyl rubber gels as a function of the immersion time in toluene after their synthesis at room temperature.

Figure 2 represents the weight swelling ratio of butyl rubber gels as a function of the sulfur monochloride concentration used in the gel preparation.

Figure 3: represents crosslinked butyl rubber beads of sizes 0.25 to 0.40 mm after their preparation by the suspension crosslinking technique at 450 rpm stirring speed.

Figure 4 represents the butyl rubber beads of Figure 3 after swelling in toluene.

Figure 5 represents crosslinked butyl rubber beads of sizes 1 to 2 mm in a dried state obtained by the suspension crosslinking technique at 300 rpm stirring speed.

EXAMPLES

In the solution crosslinking process of butyl rubber (poly (isobutylene-co-isoprene)) which leads to hydrophobic gels with high swelling capacities, the main component in the gel synthesis is butyl rubber (purchased from Exxon Chem. Co.) The butyl rubber samples Butyl 268 used in this invention contained 1.5 to 1.8mol % isoprene units,. The weight-average molecular weight and the polydispersity index of the butyl rubber samples were $3.9x10^5$ g/mol and 2.5, respectively, as determined by size exclusion chromatography with polystyrene standards (Waters, Model M - 6000A).

For the present invention, sulfur monochloride was purchased from Aldrich Co. Some of the butyl rubber gel samples were prepared with sulfur monochloride synthesized from sulfur and dry chlorine gas at 50 - 80°C according to a method described by Feher (F. Feher, "Sulfur, selenium, tellurium", in Handbook of Preparative Inorganic Chemistry, Ed. G. Brauer, Vol. 1, 2nd Ed., Academic Press, NY, 1963, p. 341). The purities of both Aldrich and home made sulfur monochlorides were higher than 98 %.

The crosslinking process of butyl rubber can be conducted by either solution or suspension crosslinking techniques. By the solution crosslinking, butyl rubber is first dissolved in an organic solvent at room temperature. The polymer concentration may vary between 4 and 10 w/v %. Then, sulfur monochloride is added into the polymer solution. The crosslinking reactions proceed at room temperature and result in the formation of soft gels. The solution crosslinking reactions can be carried out in glass tubes or, between glass plates in order to obtain butyl rubber gels in the form of rods or membranes, respectively.

By the suspension crosslinking technique, an organic solution of butyl rubber containing sulfur monochloride is suspended in an aqueous phase containing additives to form a suspension of droplets and crosslinked therein at room temperature to give products in bead form having a controlled size. The suspension crosslinking reaction is carried out under nitrogen atmosphere in reactors, fitted with a mechanical stirrer, nitrogen inlet, and outlet. The amount and the type of the additives as well as the stirring speed during the crosslinking process are varied depending on the required size of the beads.

After the preparation of the gels, they are left in an excess of toluene for at least two weeks. During this period, the post crosslinking reactions take place by the attack of pendant sulfur chloride groups to the internal vinyl groups on butyl rubber. After this period, the amount of uncrosslinked polymer, i.e., the sol fraction is less than 2% indicating the high crosslinking efficiency of sulfur monochloride.

The swelling capacity of the gels in the form of rods and membranes was measured in toluene by the gravimetric technique. For this purpose, the gel samples equilibrium swollen in toluene were weighed on an electronic balance (Sartorius BA 310 S). The weight swelling ratio q_w was calculated as

$$q_w = \left(\frac{\text{mass of the equilibrium swollen gel}}{\text{mass of the gel after synthesis}}\right)\left(\frac{\text{mass of the gel after synthesis}}{\text{mass of the dry gel}}\right) \quad \text{(1a)}$$

$$q_w = \left(\frac{m}{m_0}\right) q_F \qquad \text{(1b)}$$

where m and m_0 are the masses of the equilibrium swollen gel in toluene and the gel after synthesis, respectively, and q_F is the degree of swelling of the gel after preparation. q_F of the gels can be determined experimentally from the masses of the gel samples after synthesis and after drying, or, can also be calculated as:

$$q_F = \frac{100\, d_1}{c} + 1 \qquad \text{(1c)}$$

wherein, d_1 is the density of the solvent used in the crosslinking process (in g/ml) and c is the initial butyl rubber concentration in w/v % (weight/volume).

Applicants made various measurements using an initial butyl rubber concentration of c= 5w/v % and toluene as solvent (d_1 = 0.867 g/ml) for the gel preparation. After 15 separate measurements, applicants found that the experimental value of q_F is 18 $\pm$4.8 is comparable to its theoretical value of 18.34 calculated using equation (1c).

The swelling capacity of the gel beads was measured by the volumetric technique. The diameters of the beads after synthesis (D_0) and after equilibrium swelling in toluene (D) were measured using an image analyzing system consisting of a stereo microscope (Olympus Stereomicroscope SZ), a video camera (TK 1381 EG) and Pentium 2 PC with a data analyzing software (BS-200 BAB). The volume and the weight swelling ratios of the beads (q_v and q_w, respectively) were calculated using the following equations:

$$qv = (v_2^0)^{-1} (D/D_0)^3 \qquad (2)$$

$$q_w = 1 + \frac{(q_v - 1) d_1}{d_p} \qquad (3)$$

where

$$v_2^0 = c / 100 d_p \qquad (4)$$

wherein, d_p is the density of butyl rubber (0.917 g/ml).

One gram of the gel produced in this invention absorbs up to about 100 g of toluene, whereas this value can be adjusted by changing the sulfur monochloride or butyl rubber concentrations used in the gel preparation.

The butyl rubber samples were purified by dissolving in toluene and then precipitating into an excess of acetone at room temperature. In the following examples the weight volume ratios are given with respect to butyl rubber.

EXAMPLES 1-4

In 100 ml toluene, 1 to 10 g butyl rubber is dissolved at room temperature (See Table 1). After bubbling nitrogen for 20 minutes, a predetermined amount of sulfur monochloride is added under stirring and the solution was transferred with a syringe:

a) into several glass tubes of 5.5 mm internal diameters and about 250 mm length, and,
b) into molds of dimensions 5x5x0.1 cm^3 made using two glass plates covered with Melinex sheets (Boyden Data Papers Ltd., England) and a polyethylene gasket placed between them.

After a predetermined reaction time at room temperature (22 ± 2 °C), the gels formed are cut into specimens of approximately 10 mm in length and immersed in excess toluene at room temperature for two weeks.

The initial concentrations of butyl rubber and sulfur monochloride and swelling capacities of the resulting gels in toluene at room temperature are collected in Table 1. It is seen that one gram of the gel prepared at 4% initial butyl rubber concentration absorbs about 50 g of toluene. This value decreases as the initial concentration of butyl rubber increases. No gel forms if the butyl rubber concentration in toluene is less than 4w/v %.

TABLE 1:

Example	Butyl rubber concentration %(w/v)	S_2Cl_2 concentration %(v/w)	reaction time (days)	Equilibrium weight swelling ratio (q_w)
1	≤ 3	5	6 days	No gel formation
2	4	5	48 h	49 ± 8
3	5	5	44 h	29 ± 2
4	10	5	22 h	20.3 ± 0.5

EXAMPLES 5-19

5 g butyl rubber is dissolved in 100 ml toluene at room temperature. After bubbling nitrogen for 20 minutes, different amounts of sulfur monochloride are added under rigorous stirring. Then, the solutions are transferred into several glass tubes or into molds as described in Examples 1-4. The reaction time is set to 3 days for sulfur monochloride concentrations less than 2.5% v/w. For higher concentrations, the reactions are carried out for one day. After crosslinking reactions at room temperature (22 ± 2°C), the gels formed are cut into approximately 10 mm long specimens and immersed in excess toluene for two weeks.

During this time interval the post crosslinking reactions occur by the attack of pendant sulfur chloride groups to the internal vinyl groups on butyl rubber. This is evidenced from the decrease of the gel volume in toluene with time. The results are given in Figure 1.

In Figure 1, the equilibrium weight swelling ratios q_w of the gels are plotted as a function of their immersion time in toluene after synthesis. Initial butyl rubber concentration for the gel preparation = 5w/v %. S_2Cl_2 concentrations are indicated in the figure.

At sulfur monochloride concentrations higher than 10% v/w, the post crosslinking reactions in toluene results in a considerable decrease in the swelling capacity of the gels. At sulfur monochloride concentrations below 10% v/w, this behavior is not visible in the swelling curves.

Figure 2 shows the swelling capacities of the gels plotted as a function of the sulfur monochloride (S_2Cl_2) concentration used in the gel preparation. Initial butyl rubber concentration = 5w/v %. The data points are average of at least 6 separate experiments. The error bars show the standard deviations.

The equilibrium weight swelling ratios q_w of the gels are almost constant for S_2Cl_2 concentrations above 10%. Below this value however, q_w rapidly increases and approaches 100 at S_2Cl_2 concentrations of 0.6 to 1.0%. A continuous gel cannot form in the reaction solution below 0.6% S_2Cl_2.

EXAMPLES 20 - 35

200 ml water containing 0.5 g bentonite, 0.2 g gelatine and 0.8 g sodium chloride is introduced into a 500 ml round bottom reactor and stirred at 450 rpm under nitrogen atmosphere for 10 min. Separately, in an Erlenmeyer flask, 5 g butyl rubber dissolved in 50 ml toluene is mixed with 1 ml sulfur monochloride and nitrogen is bubbled through the organic solution for 10 minutes. Then, the toluene solution is transferred into the reactor and the reaction is allowed to proceed for 8 hours at room temperature (22 ± 2°C) under nitrogen atmosphere.

After polymerization, the beads are separated from the water phase and washed several times, namely first with water, then with acetone and finally with toluene, always in excess amount. Then the beads are left in excess toluene for two weeks, toluene is refreshed every two days. The beads are then dried at 50°C in vacuum until constant weight. After synthesis, more than 80% of the beads are between 0.25 to 0.4 mm.

An optical micrograph of the beads taken respectively after their preparation in water and after swelling in toluene are shown in Figures 3 and 4. In order to make the beads visible under microscope, the beads have been colored with a phthalocyanine dye. Figure 5 shows the beads of sizes 1 to 2 mm in a dried state obtained at 300 rpm stirring speed.

The gel beads obtained at different initial butyl rubber and sulfur monochloride concentrations, exhibit swelling capacities comparable to those obtained by solution crosslinking experiments (See Table 1 and Figure 2).

CLAIMS

1) Superabsorbent materials in the form of polymer gels based on butyl rubber, characterized in that they are hydrophobic, they float on water and have a swelling capacity up to about 100 gram of a suitable organic solvent per gram of dry material.

2) Superabsorbent materials according to claim 1, characterized in that they are in the form of membranes, rods or beads.

3) Superabsorbent materials according to claim 1, characterized in that they are in the form of mono-disperse, spherical gel beads in the size range of 0.1 to 2 mm in diameter.

4) A suspension crosslinking process for the production of superabsorbent materials according to any one of claims 1 to 3, characterized in that a homogeneous solution of butyl rubber in an organic solvent is prepared under nitrogen atmosphere, then sulfur monochloride is added into the polymer solution, this solution is added by stirring into an aqueous solution, optionally containing additives, to obtain an oil-in-water suspension and the discontinuous oil phase is crosslinked at constant stirring rate and spherical gel beads are obtained.

5) A solution crosslinking process for the production of superabsorbent materials according to any one of claims 1 and 2, characterized in that a homogeneous solution of butyl rubber in an organic solvent under nitrogen atmosphere is prepared, then crosslinked with sulfur monochloride and polymer gels in the form of rods and membranes are obtained.

6) Process according to any one of claims 4 or 5, characterized in that the crosslinking is made at room temperature.

7) Process according to any one of claims 4 to 6, characterized in that the butyl rubber concentration is at most 11w/v %, preferably between 3.5 and % 10 w/v, especially 5w/v %.

8) Process according to any one of claims 4 to 7, characterized in that the sulfur monochloride concentration is between 0.6 and 80%, preferably between 0.6 and 5.0% and especially between 0.6 and 1.0.

9) Process according to any one of claims 4 to 8, characterized in that the stirring rate is at least 100 rpm, preferably between 200 and 700 rpm and especially 300 rpm.

10) Process according to any one of claims 4 to 9, characterized in that the organic solvent is a solvent with a solubility parameter close to that of butyl rubber, like chloroform, benzene, toluene, xylene, carbon tetrachloride and cyclohexane.

11) Process according to any one of claims 4 to 10, characterized in that the aqueous solution contains one or more additives chosen from the group consisting of a) sodium chloride, potassium chloride and b) alkaline earth phosphates, carbonates and silicates, starch, gelatin, poly (vinyl alcohol); poly (acrylic acid) and its salts; poly (vinyl pyrrolidone).

12) Use of the superabsorbent materials according to claims 1 to 3 for treatment of oil containing wastewater.

13) Use of the superabsorbent materials coming from a waste water treatment according to claim 12 as a fuel.

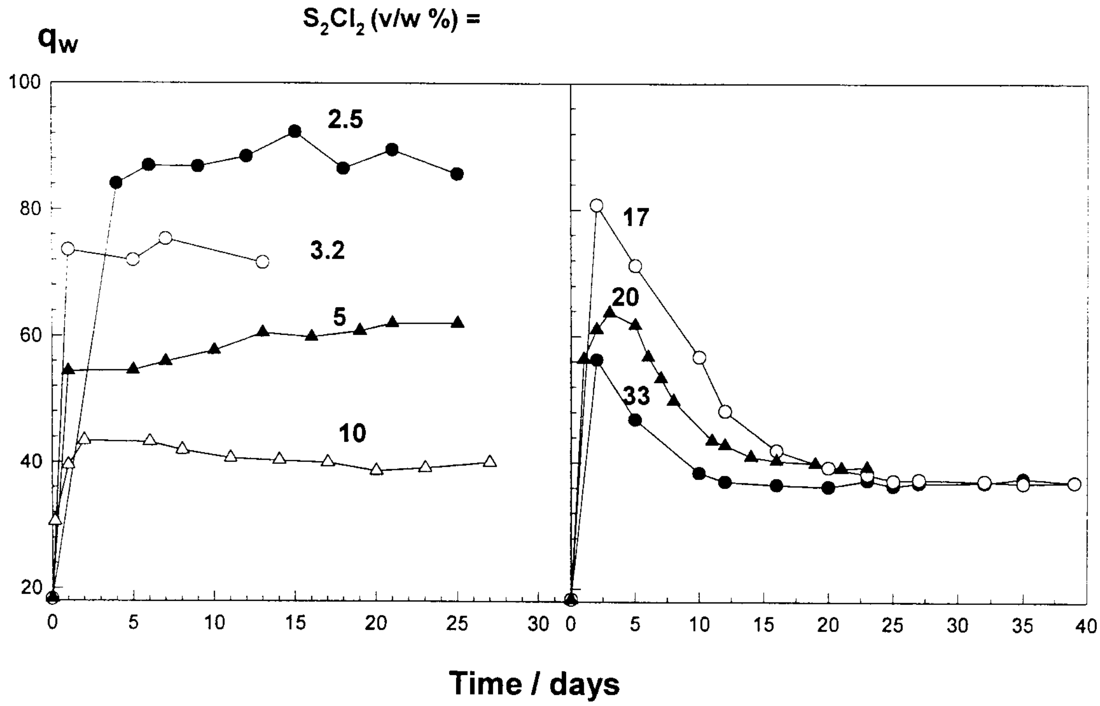


Fig. 1

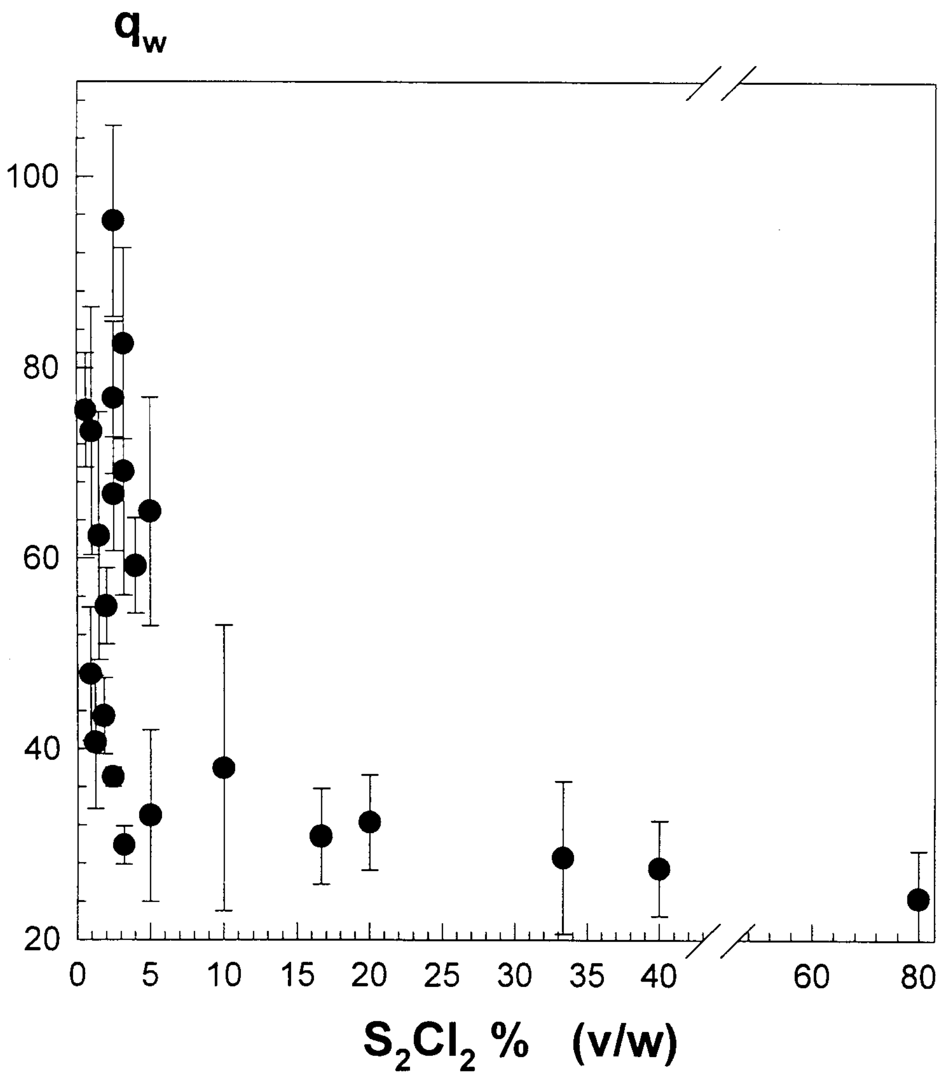


Fig. 2

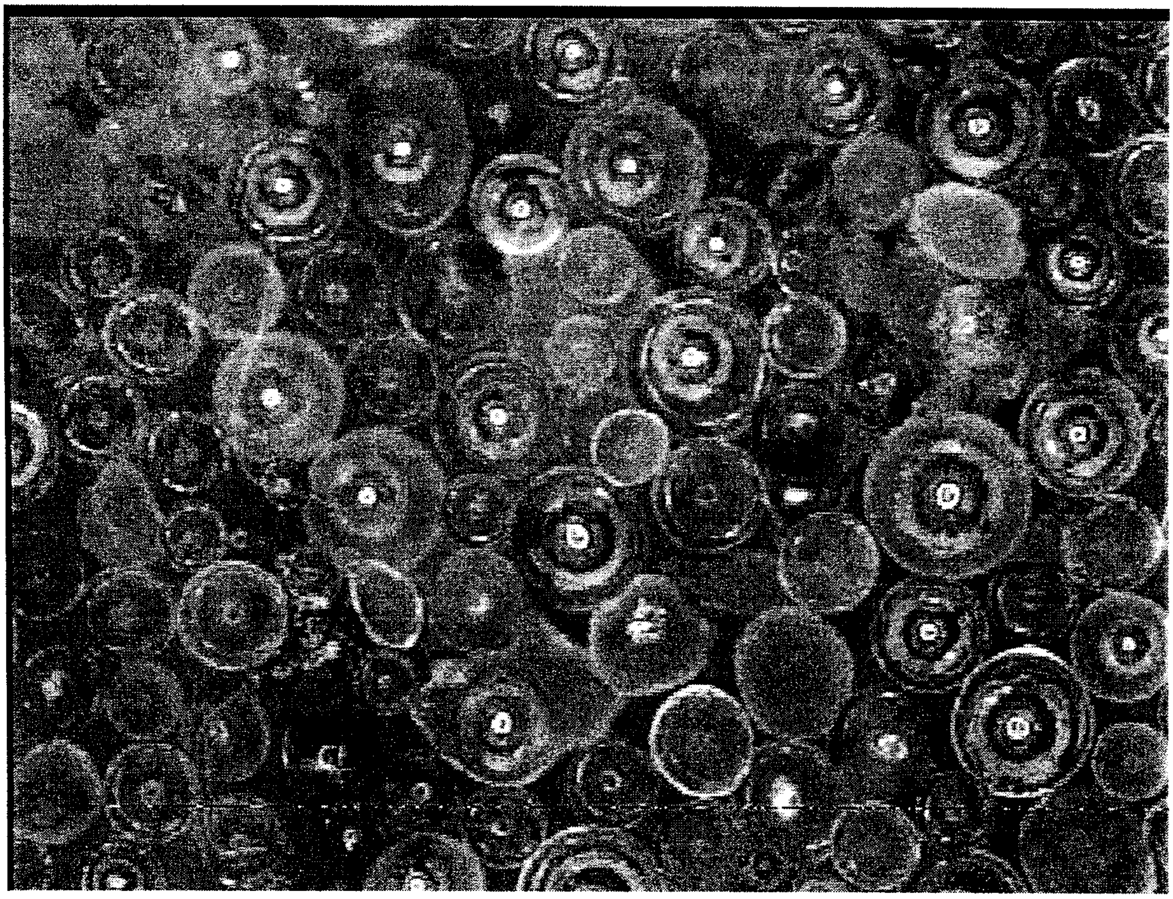


Fig.3

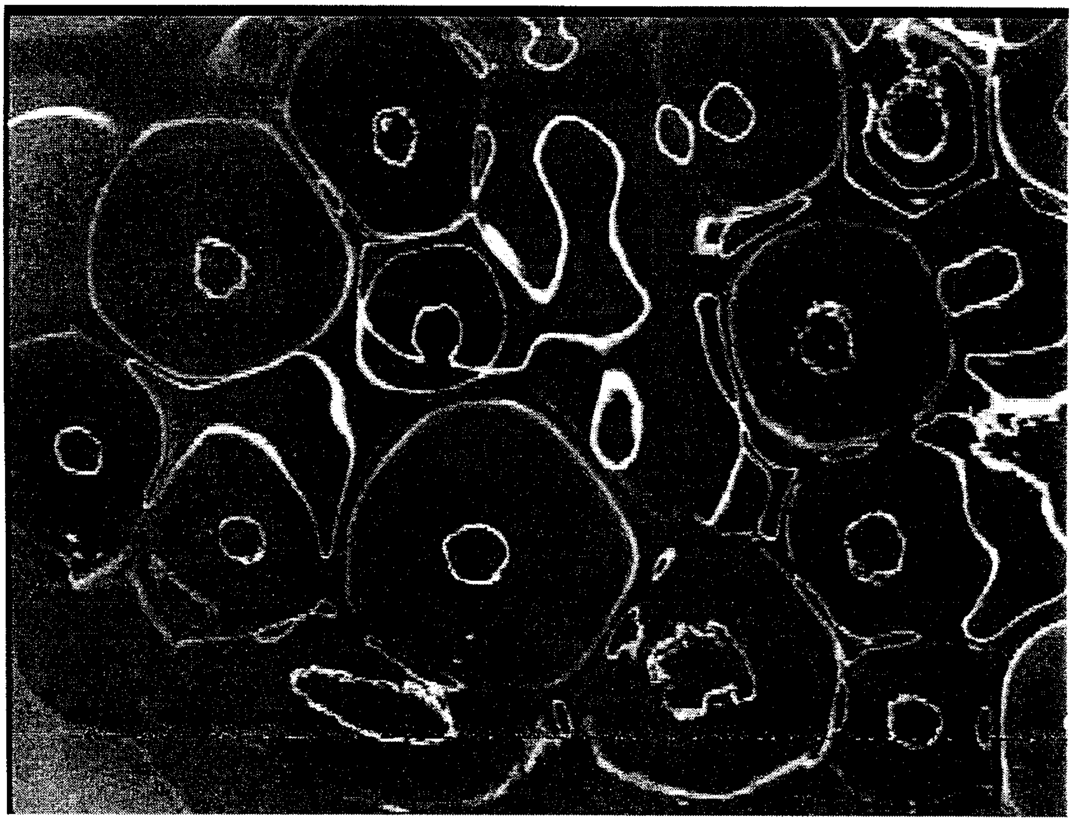


Figure 4

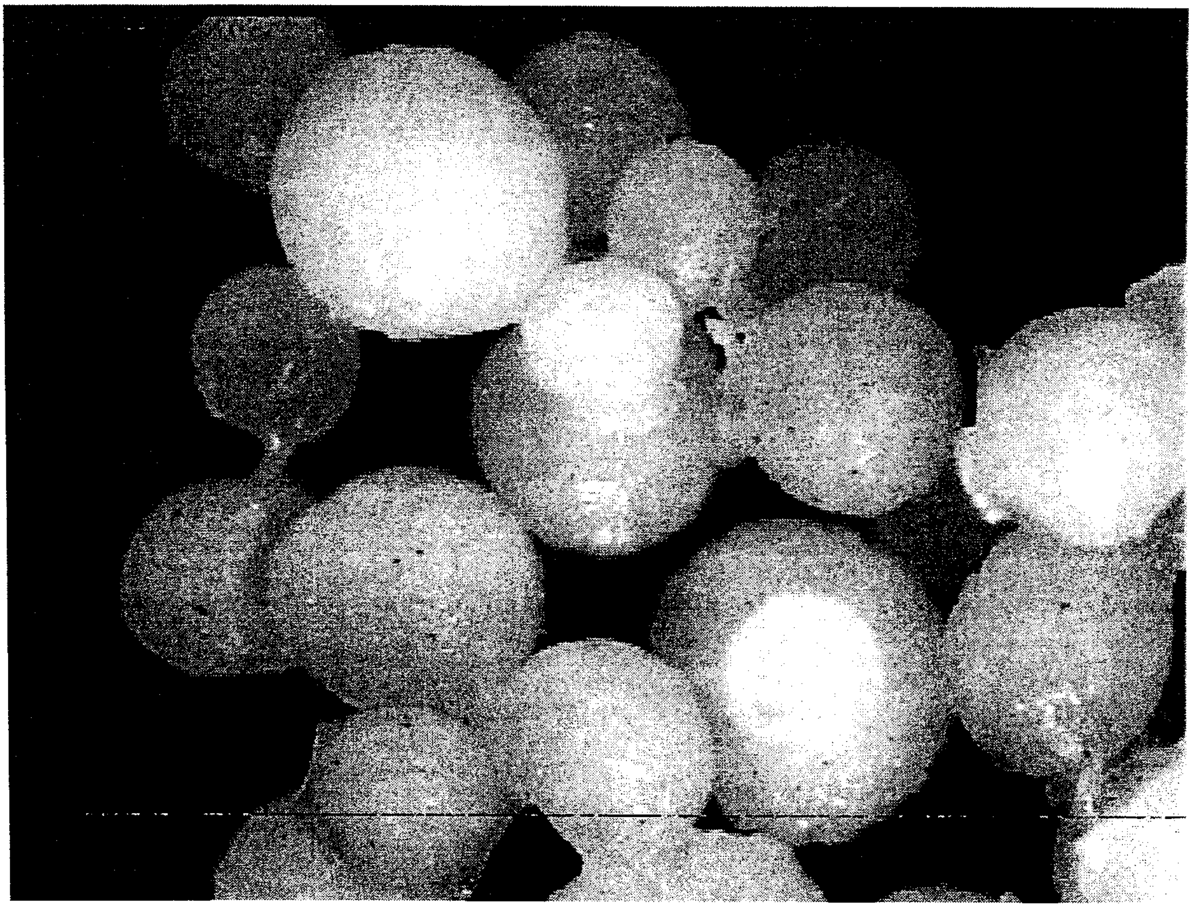


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/TR 99/00055

CLASSIFICATION OF SUBJECT MATTER

IPC[7]: C 08 F 10/10; C 08 L 23/22; C 08 J 3/24; B 01 J 20/26; C 02 F 1/28

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)

IPC[7]: C 08 F; C 08 L; C 08 J; B 01 J; C 02 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI Database, Derwent Publications Ltd., London (GB), EPO PAJ Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 62049914 A (NIPPON ZEON KK) 4 March 1987 (04.03.87) (abstract), World Patents Index [online]. London, U.K.: Derwent Publications, Ltd. [retrieved on 19.05.00]. Accession No. 1987-103992, Derwent Week 198715, Retrieved from: EPO WPI Database.	1-13
A	JP 11342509 A (MITSUBOSHI BELTING LTD) 14 December 1999 (14.12.99) (abstract) World Patents Index [online]. London, U.K.: Derwent Publications, Ltd. [retrieved on 19.05.00]. Accession No. 2000-101921, Derwent Week 200009, Retrieved from EPO WPI Database.	1-13
A	JP 9302045 A (NIPPON GOSEI GOMU KK) 25 November 1997 (25.11.97) (abstract) World Patents Index [online]. London, U.K.: Derwent Publications, Ltd. [retrieved on 19.05.00]. Accession No. 1998-059227, Derwent Week 199806, Retrieved from: EPO WPI Database.	1-13

☐ Further documents are listed in the continuation of Box C. ☒ 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
26 May 2000 (26.05.2000)	11 August 2000 (11.08.2000)

Name and mailing adress of the ISA/AT	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/TR 99/00055

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP A2 62049914	04-03-1987	none	
JP A2 11342509	14-12-1999	none	
JP A2 9302045	25-11-1997	none	