

PATENT SPECIFICATION

(11) 1 567 290

1 567 290

- (21) Application No. 4487/78 (22) Filed 3 Feb. 1978
 (31) Convention Application No. 52/016 834
 (32) Filed 17 Feb. 1977 in
 (33) Japan (JP)
 (44) Complete Specification published 14 May 1980
 (51) INT CL³ C08F 14/06, 2/18
 (52) Index at acceptance C3P JG
 (72) Inventors TAKESHI SEKIHARA, TOMOYUKI EMURA and
 MASAYUKI MURASHIGE



(54) PREPARATION OF VINYL CHLORIDE POLYMERS

(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED of 15 Kitahama-5-chome, Higashi-ku, Osaka, Japan, a Japanese Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of vinyl chloride polymers and specifically to such a process carried out in an aqueous medium in the presence of certain polycyclic nitrogen-containing compounds which have the effect of preventing the formation of scale on the inner wall of the reactor in which the process is carried out.

It is well-known that the traditional suspension or emulsion polymerization of monomer comprising vinyl chloride in an aqueous medium results in the formation of a thin film or scale deposit of polymer adhering to the wall of the polymerization vessel or to the blade of the stirrer; such deposits are hereafter referred to simply as "scale". The scale lowers the cooling capacity of the polymerization vessel and, moreover, contaminates and thus markedly reduces the quality of the vinyl chloride polymer produced, as can be seen by the appearance of so-called "fish eyes". In order to overcome these problems, it is necessary that, after discharge of the polymerization mixture from the polymerization vessel, the polymerization vessel should be cleaned completely before commencing further polymerization. However, this cleaning is labour-intensive and consumes considerable time, which significantly decreases the production capacity of the vessel. Moreover, the way in which the scale is cleaned from the vessel is, by scratching it off by hand by a workman inside the vessel: this operation is very dangerous and insatiable.

Ideally, therefore, the polymerization should be carried out in such a way as to avoid or to minimize the formation of scale on the wall of the vessel and many methods of

achieving this have been proposed. For example, Japanese Patent Publication No. 37988/70 discloses a process for the suspension polymerization of vinyl chloride in which an aqueous system containing vinyl chloride or a mixture of vinyl chloride and a monomer copolymerizable therewith is first converted to a dispersion system using a dispersing agent, for example a cellulose derivative or a mixture thereof with another dispersing agent. The pH value of the dispersion system is then adjusted to at least 8 by adding an alkali metal oxide or hydroxide. The system is then subjected to suspension polymerization. Although this process certainly has some success in reducing scale formation, it is not sufficiently effective for industrial use.

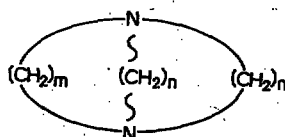
Other processes have been employed in which an additive designed to reduce scale formation is incorporated in the polymerization system. For example, Japanese Patent Publication No. 40462/72 and Japanese Patent Application No. 44276/75, as laid-open to public inspection, have proposed such a process using a nitrite as the additive and Japanese Patent Publication No. 4753/71 describes such a process in which the additive is a compound having an azine ring. These processes have been found to be very effective in preventing scale formation, but they have the disadvantage that they produce a polymer having much inferior thermal stability and it is, therefore, difficult to employ them on an industrial scale.

Another approach to the problem is to coat the wall of the polymerization vessel with a suitable material and a considerable number of different materials have been proposed for this purpose. For example, U.S. Patent Specification No. 3,669,946 describes a process in which the walls are coated with a dye, a pigment or a compound having an azine ring. These processes, however, also give rise to difficulties. Thus, the procedure in which a dilute solution of the coating material has to be coated uniformly over the whole wall of the polymerization vessel and then dried is troublesome and time-con-

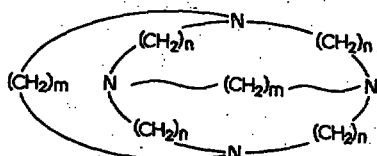
suming. Moreover, the coating material tends to dissolve to some extent in the monomer during the polymerization and thus has to be replaced after several batch polymerizations. Furthermore, the coating material dissolved in the monomer contaminates the polymer produced, thus adversely affecting its properties, particularly thermal stability.

We have now discovered a process for polymerizing monomer comprising vinyl chloride by the use of an additive which substantially prevents scale formation without damaging the properties of the polymer produced.

Thus, the present invention consists in a process for preparing a vinyl chloride polymer by polymerizing monomer comprising vinyl chloride in an aqueous medium and in the presence of a polycyclic nitrogen-containing compound of formula



and/or



in which m and n are each 1, 2 or 3, the amount of said nitrogen-containing compound being from 1 to less than 100 ppm based on the weight of said monomer.

The mechanism whereby scale adheres to the wall of a polymerization vessel during suspension polymerization of vinyl chloride, and hence the mechanism whereby the nitrogen-containing compounds of the invention prevent this adhesion of scale, are not always clear. However, it is believed that scale formation in a conventional vinyl chloride polymerization process is caused by the following sequence of events: as the polymerization progresses, a small quantity of hydrogen chloride is generated and this dissolves in the aqueous medium, giving rise to chloride ions; these ions corrode the wall of the polymerization vessel, damaging its smoothness and, for example, causing pitting corrosion; as a result, active sites to which scales can conveniently attach are produced on the surface. Although we do not wish to be limited by any theory, it is believed that the polycyclic nitrogen-containing compounds used in the present invention, which have a cage-like molecular structure, are strongly adsorbed on the active sites via the unpaired

electron on the bridgehead tertiary nitrogen atom of the compound; thus adsorption of chloride ions and, in turn, attachment of scale are inhibited because of steric hindrance by the cage-like molecular structure of the nitrogen-containing compound.

Examples of suitable polycyclic nitrogen-containing compounds which may be used in the present invention include: 1,4 - diazabicyclo[2.2.2]octane; 1,5 - diazabicyclo[3.2.2]nonane; 1,3,5,7 - tetraazaadamantane; and 1,3,6,8 - tetraazatricyclo[4.4.1.1^{3,8}]-dodecane. A single one of these compounds or a combination of two or more thereof may be used. The amount of the nitrogen-containing compound or compounds employed may vary from 1 ppm to less than 100 ppm by weight, preferably from 1 to 70 ppm by weight and more preferably from 5 to 50 ppm by weight, based on the weight of monomer. If the amount of this compound is less than 1 ppm, it does not sufficiently prevent scale formation and a film-like scale starts to be produced on the wall of the polymerization vessel. On the other hand, if the amount added is 100 ppm or more, it tends to retard polymerization and lowers the thermal stability of the polymer produced.

The polycyclic nitrogen-containing compound or compounds may be added to the polymerization system all at once before the polymerization begins or part of the compound may be added before polymerization and the remaining part added as a solution by spraying it into the vapour phase on the inner wall of the polymerization vessel during polymerization.

The process of the invention may be applied to suspension or emulsion polymerization processes in aqueous media, although its effect is particularly noticeable in suspension polymerization.

In the process of the invention as applied to suspension polymerization, the oil-soluble catalysts and suspension stabilizers commonly used in the suspension polymerization of vinyl chloride may be employed. Examples of suitable oil-soluble catalysts include: diacyl peroxides, e.g. lauroyl peroxide; alkyl peroxyesters, e.g. t-butyl peroxyvalerate; dialkyl peroxydicarbonates, e.g. diisopropyl peroxydicarbonate; acetylalkyl peroxides, e.g. acetylcyclohexylsulphonyl peroxide; and azo-type catalysts, e.g. azobis(2,4-dimethylvaleronitrile); it is also possible to use mixtures of two or more such catalysts. The amount of catalyst used is, as in conventional suspension polymerization, generally from 0.005 to 0.5% by weight, based on the weight of the monomer. Examples of suitable suspension stabilizers include: water-soluble synthetic high molecular weight compounds, e.g. partially saponified polyvinyl alcohol; cellulose derivatives, e.g. hydroxypropyl methyl-

cellulose; and natural high molecular weight compounds, e.g. gelatin.

In the process of the present invention as applied to emulsion polymerization, water-soluble catalysts and emulsifiers as used in conventional emulsion polymerization processes may be used. Examples of water-soluble catalysts include: persulphates, e.g. potassium persulphate; hydrogen peroxide; and redox catalysts comprising these peroxides and a reducing agent. Examples of emulsifiers include anionic surface active agents, such as alkali metal alkyl sulphates, e.g. sodium lauryl sulphate; and alkali metal alkylarylsulphonates, e.g. sodium dodecylbenzenesulphonate.

The polymerization process of the present invention is preferably carried out at temperature from 40°C to 80°C and, if desired, it may be carried out in the presence of chain transfer agents or cross-linking agents.

The process of the invention may be carried out as a homopolymerization process in which the monomer to be polymerized consists solely of vinyl chloride, to produce vinyl chloride homopolymer, or it may be carried out as a copolymerization process, in which the vinyl chloride is copolymerized with one or more copolymerizable monomers to produce a vinyl chloride copolymer. Examples of copolymerizable monomers include: α -olefins, e.g. ethylene and propylene; vinyl halides other than vinyl chloride; vinylidene halides, e.g. vinylidene chloride; vinyl ethers, e.g. methyl vinyl ether and lauryl vinyl ether; and vinyl esters, e.g. vinyl acetate. Where they are employed, such comonomers are generally used in an amount not greater than 30% by weight, preferably not greater than 15% by weight, based on the total weight of monomer.

The process of the invention can be carried out using conventional polymerization vessels, i.e. glass-lined vessels or stainless steel vessels, and we have found that the scale-reducing effect achieved by the invention is most noticeable when using stainless steel vessels.

By carrying out the process of the invention as described above, it is possible to prevent any substantial formation of scale without causing any deterioration in the properties, e.g. thermal stability, of the vinyl chloride polymer produced. As a result, after discharging the contents from the polymerization vessel, cleaning of the vessel can be achieved very easily. It is possible to clean the vessel quite adequately merely by washing the wall surface with a jet of low pressure water, e.g. at a pressure of 50 kg/cm² or less. Consequently, the process of the invention is thought to be of considerable industrial importance.

The invention is further illustrated by the following non-limiting Examples. In these

Examples, the state of scale attachment, the number of fish eyes, the initial discolouration and the thermal stability were evaluated by the following test methods.

State of scale attachment

After the polymerization has been completed, the contents of the polymerization vessel are discharged. The polymer and scale attached to the wall of the vessel are washed off by a jet of water at a pressure of 15 kg/cm² and the material washed off is weighed. Thereafter, the scale which could not be washed off by this low pressure water is scraped off manually using a scraper and the material scraped off is weighed. The total weight of polymer and scale removed by the low pressure water is reported as the weight (A) and the weight of scale scraped off manually is shown as the weight (B). The weight (A) includes the weight of polymer which normally looses adheres to the wall of the vessel; however, the weight (B) indicates the weight of real scale strongly adhering to the vessel wall.

Fish eyes

50 g of the vinyl chloride polymer, 25 g of dioctyl phthalate 0.5 g of barium stearate and 0.5 g of cadmium stearate are thoroughly mixed in a beater at room temperature. The mixture is then kneaded on a roll mill at 150°C for 7 minutes and formed into a film of thickness 0.15 mm. The number of fish eyes per 100 cm² of film is counted.

Initial discolouration

A compound consisting of 100 parts by weight of the vinyl chloride polymer, 1 part by weight of a calcium-zinc type composite stabilizer (Mark-37 produced by Adekaargus Chemical Company Limited) 2 parts by weight of epoxidized soybean oil (Adekacizer 0 130P, produced by Adekaargus Chemical Company Limited) and 1 part by weight of stearic acid is formed into a sheet by kneading on a roll mill for 5 minutes at 160°C and pressing for 5 minutes at 170°C. The degree of discolouration of the sheet is visually observed and classified as follows:

A = Standard
B = Slightly inferior
C = Very poor

Thermal stability

The compound employed in the test for initial discolouration is formed into a sheet by kneading and pressing under the same conditions as are used in the test for initial discolouration. The sheet is then heated at 180°C in a Geer's oven. The thermal stability is expressed as the time required for the sheet to turn black.

EXAMPLES 1 and 2 and

COMPARATIVE EXAMPLES 1 to 3.

Into a 100 litre stainless steel polymerization vessel were charged 45 kg of deionized water, 30 g of polyvinyl alcohol (degree of saponification 80%, mean degree of polymerization 1700), 7.5 g of di-t-butylcyclohexyl peroxydicarbonate, and 1,4-diazabicyclo[2.2.2]octane in the amount shown in Table 1.

The air was then evacuated from the vessel, after which 30 kg of vinyl chloride were charged into the vessel and polymerized, with stirring, at 57°C. The pressure in the

vessel at the beginning of the polymerization

was 8.7 kg/cm² gauge. When the pressure

reduced to 6.7 kg/cm² gauge, the polymeri-

zation was stopped and unreacted vinyl

chloride monomer was recovered. The con-

tents of the vessel were then discharged and

dried to give a vinyl chloride polymer having

a mean degree of polymerization of 1100 at

a conversion of 85%.

The properties of the polymer and the ease

of removal of scale from the vessel walls were

determined, and the results are also shown

in Table 1.

TABLE 1

	Additive		Polymerization time (hr)	Amount of scale attached (g/m ²)	
	Kind	Amount added (ppm)		(A) Immediately after discharge of the contents	(B) After cleaning by a jet of low-pressure water of 15 kg/cm ²
Comparative example 1	Not added	0	6.5	250	110
Comparative example 2	1,4-Diazabicyclo[2.2.2]octane	0.3	6.5	130	30
Example 1	"	10	6.7	30	0
Example 2	"	30	7.0	20	0
Comparative example 3	"	300	11.5	20	0

TABLE 1 (Continued)

	Particle size distribution (weight percent)			Fish eye (Number/100 cm ²)	Initial discoloration	Thermal stability (min.)
	42-Mesh* through	100-Mesh* through	250-Mesh* through			
Comparative example 1	99.7	71.2	0.5	750	A	60
Comparative example 2	99.5	73.5	0.3	64	A	60
Example 1	99.8	71.8	0.7	3	A	55
Example 2	98.7	72.7	0.3	1	A	50
Comparative example 3	97.3	76.8	0.9	5	B	40

*Mesh standard is Tyler.

In Examples 1 and 2, which were carried out in accordance with the process of the present invention, there was very little polymer adhering to the walls of the vessel after discharge of the contents and this material could be removed easily and completely by a jet of low pressure water at a pressure of 15 kg/cm². Furthermore, the vinyl chloride polymers obtained in these Examples had excellent properties, as may be seen from the particle size distribution, fish eye test and initial discoloration and thermal stability tests, whose results are reported in Table 1.

On the other hand, in Comparative Examples 1 and 2, where no polycyclic nitrogen-containing compound was present or it was present in too small a quantity, a considerable quantity of scale was attached to the polymerization vessel walls and the results of the

fish eye test were inferior. Moreover, in Comparative Example 3, in which the amount of polycyclic nitrogen-containing compound exceeded that required by the process of the present invention, although scale formation was prevented, the polymerization time was much prolonged and the initial discoloration and thermal stability were found to be relatively poor.

EXAMPLES 3 to 5 and
COMPARATIVE EXAMPLES 4 to 6.

Into a 100 litre stainless steel polymerization vessel were charged 45 kg of deionized water, 30 g of polyvinyl alcohol (degree of saponification 80%, mean degree of polymerization 1700), 9 g of α,α' -azobis(2,4-dimethylvaleronitrile) and the additive shown in Table 2 in the amount shown there. The

vessel was then evacuated, after which 30 kg of vinyl chloride monomer were charged into the vessel and polymerized, with stirring, at 64°C. The pressure in the polymerization vessel when polymerization began was 10.2 kg/cm² gauge. When the pressure dropped to 7.2 kg/cm² gauge, the polymerization was stopped and the unreacted vinyl chloride monomer was recovered. The contents of the

vessel were then discharged and dried to give 10 a vinyl chloride polymer having a mean degree of polymerization of 850 at a conversion of 90%.

The amount of scale adhering to the walls of the polymerization vessel, the number of fish eyes, the initial discoloration and the thermal stability were determined and the results are also shown in Table 2.

TABLE 2

	Additive		Polymerization time (hr)	Amount of scale attached (g/m ²)	
	Kind	Amount added (ppm)		(A) Immediately after discharge of the contents	(B) After cleaning by a jet of low pressure water of 15 kg/cm ²
Example 3	1,5-Diazabicyclo[3, 2, 2]nonane	10	7.7	50	0
Example 4	1,3,6,8-Tetraazatricyclo[4,4,1,1 ^{3,6}]dodecane	10	7.3	10	0
Example 5	1,3,5,7-Tetraazaadamantane	10	8.0	30	0
Comparative example 4	Ti-n-amine	10	18.0	350	150
Comparative example 5	Morpholine	10	8.5	110	20
Comparative example 6	Sodium hydroxide	300	10.8	250	10

TABLE 2 (Continued)

	Particle size distribution (weight percent)			Fish eye (Number/100 cm ²)	Initial discoloration	Thermal stability (min.)
	42-Mesh* through	100-Mesh* through	250-Mesh* through			
Example 3	99.3	70.0	0.1	15	A	55
Example 4	99.8	68.3	0.2	1	A	60
Example 5	98.5	65.2	0.8	27	A	50
Comparative example 4	89.2	35.7	6.7	1200	C	40
Comparative example 5	93.7	71.3	0.5	300	C	35
Comparative example 6	53.9	26.3	10.8	1500	C	40

*Tyler

In Examples 3 to 5, which were carried out in accordance with the process of the present invention, the amount of polymer adhering to the walls of the reaction vessel after discharge of the contents was extremely small and this material could easily be removed by means of a jet of low pressure water. Furthermore, the vinyl chloride polymers obtained had excellent properties, as can be seen by the particle size distribution, number of fish eyes, initial discoloration and thermal stability reported in Table 2. On the other hand, in Comparative Example 4, in which a tertiary amine, tri-n-amyamine, was used in place of the polycyclic nitrogen-containing compounds of the invention, scale formation was not prevented

and the results of the fish eye test were inferior. In Comparative Examples 5 and 6, where morpholine and sodium hydroxide were used, scale attachment was reduced to some extent but the results of the particle size distribution, fish eye, initial discoloration and thermal stability tests were all extremely poor.

EXAMPLE 6.

Into a 100 litre stainless steel polymerization vessel were charged 45 kg of deionized water, 24 g of potassium per sulphate, 80 g of sodium lauryl sulphate and 1.7 g of 1,3,5,7-tetraazaadamantane. After the vessel had been evacuated, 34 kg of vinyl chloride monomer were charged into it and poly-

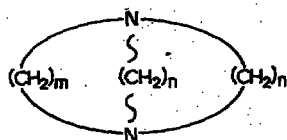
merized, with stirring, at 53°C. When the pressure in the reaction vessel had reduced by 1 kg/cm² the polymerization was stopped, unreacted vinyl chloride monomer was recovered and the contents of the vessel were discharged. The resulting vinyl chloride polymer had a mean particle size of 0.4 μ and was obtained in the form of a latex. After discharge of the contents of the vessel, the amount of scale adhering to the walls of the vessel was only 170 g/m² and this was reduced to only 7 g/m² after the vessel had been cleaned by means of a jet of low pressure water at 15 kg/cm².

15 COMPARATIVE EXAMPLE 7.

The procedure described in Example 6 was repeated, except that the 1,3,5,7 - tetraazaadamantane was omitted. A vinyl chloride polymer having a mean particle size of 0.4 μ was obtained in the form of a latex. After the contents of the vessel had been discharged, however, the amount of scale adhering to the wall of the vessel was 500 g/m² and 150 g/m² of this scale still remained attached to the wall surface even after the vessel had been cleaned by a jet of low pressure water at 15 kg/cm².

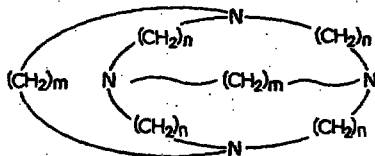
WHAT WE CLAIM IS:—

- 30 1. A process for preparing a vinyl chloride polymer by polymerizing monomer comprising vinyl chloride in an aqueous medium and in the presence of a polycyclic nitrogen-containing compound of formula



35

and/or



in which m and n are each 1, 2 or 3, the amount of said nitrogen-containing compound being from 1 to less than 100 ppm based on the weight of said monomer.

2. A process according to Claim 1, in which the amount of said polycyclic nitrogen-containing compound is from 1 to 70 ppm.

3. A process according to Claim 2, in which the amount of polycyclic nitrogen-containing compound is from 5 to 50 ppm.

4. A process according to any one of the preceding Claims, in which said polycyclic nitrogen-containing compound is 1,4 - diazabicyclo[2.2.2]octane, 1,5 - diazabicyclo[3.2.2]nonane, 1,3,5,7 - tetraazaadamantane or 1,3,6,8 - tetraazatricyclo[4.4.1.1^{0,4}]-dodecane.

5. A process according to any one of the preceding Claims, carried out as a suspension polymerization process.

6. A process according to any one of Claims 1 to 4, carried out as an emulsion polymerization process.

7. A process according to any one of the preceding Claims, effected in a polymerization vessel made of stainless steel.

8. A process according to any one of the preceding Claims, in which said monomer consists of vinyl chloride to produce a vinyl chloride homopolymer.

9. A process according to any one of Claims 1 to 7, in which said monomer comprises vinyl chloride and a copolymerizable monomer to produce a vinyl chloride copolymer.

10. A process according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

11. A vinyl chloride polymer when produced by a process according to any one of the preceding Claims.

MARKS & CLERK,
Chartered Patent Agents,
57—60 Lincoln's Inn Fields,
London WC2A 3LS.
Agents for the Applicants.



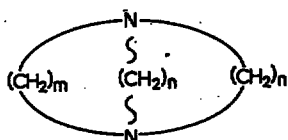
merized, with stirring, at 53°C. When the pressure in the reaction vessel had reduced by 1 kg/cm² the polymerization was stopped, unreacted vinyl chloride monomer was recovered and the contents of the vessel were discharged. The resulting vinyl chloride polymer had a mean particle size of 0.4 μ and was obtained in the form of a latex. After discharge of the contents of the vessel, the amount of scale adhering to the walls of the vessel was only 170 g/m² and this was reduced to only 7 g/m² after the vessel had been cleaned by means of a jet of low pressure water at 15 kg/cm².

15 COMPARATIVE EXAMPLE 7.

The procedure described in Example 6 was repeated, except that the 1,3,5,7 - tetraazaadamantane was omitted. A vinyl chloride polymer having a mean particle size of 0.4 μ was obtained in the form of a latex. After the contents of the vessel had been discharged, however, the amount of scale adhering to the wall of the vessel was 500 g/m² and 150 g/m² of this scale still remained attached to the wall surface even after the vessel had been cleaned by a jet of low pressure water at 15 kg/cm².

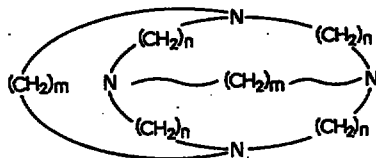
WHAT WE CLAIM IS:—

1. A process for preparing a vinyl chloride polymer by polymerizing monomer comprising vinyl chloride in an aqueous medium and in the presence of a polycyclic nitrogen-containing compound of formula



35

and/or



in which m and n are each 1, 2 or 3, the amount of said nitrogen-containing compound being from 1 to less than 100 ppm based on the weight of said monomer.

2. A process according to Claim 1, in which the amount of said polycyclic nitrogen-containing compound is from 1 to 70 ppm.

3. A process according to Claim 2, in which the amount of polycyclic nitrogen-containing compound is from 5 to 50 ppm.

4. A process according to any one of the preceding Claims, in which said polycyclic nitrogen-containing compound is 1,4 - diazabicyclo[2.2.2]octane, 1,5 - diazabicyclo[3.2.2]nonane, 1,3,5,7 - tetraazaadamantane or 1,3,6,8 - tetraazatricyclo[4.4.1.1^{3,5}]-dodecane.

5. A process according to any one of the preceding Claims, carried out as a suspension polymerization process.

6. A process according to any one of Claims 1 to 4, carried out as an emulsion polymerization process.

7. A process according to any one of the preceding Claims, effected in a polymerization vessel made of stainless steel.

8. A process according to any one of the preceding Claims, in which said monomer consists of vinyl chloride to produce a vinyl chloride homopolymer.

9. A process according to any one of Claims 1 to 7, in which said monomer comprises vinyl chloride and a copolymerizable monomer to produce a vinyl chloride copolymer.

10. A process according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

11. A vinyl chloride polymer when produced by a process according to any one of the preceding Claims.

MARKS & CLERK,
Chartered Patent Agents,
57—60 Lincoln's Inn Fields,
London WC2A 3LS.
Agents for the Applicants.