TH OF AUSTRALIA

Patents Act

ON FOR A PATENT

X/We (d) SOLVAY & CIE; 31043/m

of (c) 33, rue du Prince Albert, B-1050 Brussels, Belgium;

hereby apply for the grant of a Patent for an invention entitled

(d) "PROCESS FOR THE POLYMERISATION, IN AQUEOUS SUSPENSION, OF HALOGEN-CONTAINING VINYL MONOMERS"

which is described in the accompanying (e) complete specification.

(Note: The following paragraph applies only to Convention applications)

This application is a Convention application based on the basic application(s) for a patent or similar protection identified by number, country, and filing date as follows:

(f) 76 309. Luxembourg. 1st December, 1976.

Address for Service: PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
37-41 Queen Street
Melbourne, Australia

Dated (g) 15th November, 1977.

(h) PHILLIPS ORMONDE AND FITZPATRICK,
Attorneys for:
SOLVAY & CIE.

PHILLIPS, ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
DECLARATION FOR A PATENT APPLICATION

31043/77

In support of the (a) convention (b) application made by

SOLVAY & CIE.

(hereinafter called "applicant") for a patent (e)

for an invention entitled (d)

"PROCESS FOR THE POLYMERISATION, IN AQUEOUS SUSPENSION, OF HALOGEN-CONTAINING VINYL MONOMERS"

I/\(\text{(e)}\) Jacques VIRIOT, Director of SOLVAY & Cie, 33, Rue du Prince Albert, B-1050 Brussels (Belgium)

do solemnly and sincerely declare as follows:

1. I am \(\text{authorized}\) to make this declaration on behalf of the applicant(s).

2. We are the actual inventor(s) of the invention.

3. DANIEL TYTGAT of Avenue d'Avril, 14 B-1150 Brussels, Belgium; and STEPHANE NOEL of Poddegemstraat, 13, B-1850 Grimbergen, Belgium; and LUCIEN CLERBOIS of Avenue Sainte-Anne 130 B-1800 Vilvoorde, Belgium.

are \(\text{the actual inventor(s)}\) of the invention and the facts upon which the applicant(s) is/\(\text{are}\) entitled to make the application are as follows:

"Applicant is the assignee of the invention from the actual inventors."

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based is/\(\text{are}\) identified by country, filing date, and basic applicant(s) as follows:

Luxembourg.

1st December, 1976.

SOLVAY & CIE.

4. The basic application(s) referred to in paragraph 3 hereof was/\(\text{are}\) the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared \(\text{at}\) \(\text{Brussels, Belgium.}\)

Dated \(\text{9th November, 1977.}\)

\(\text{ADMINISTRATEUR}\)

\(\text{NEMBRE DU COMITE EXECUTIF}\)

To: The Commissioner of Patents
1. Process for the polymerisation, in aqueous suspension, of halogen-containing vinyl monomers, using lipo-soluble initiators which generate free radicals, in the presence of an effective amount of an inhibitor of crust formation derived from a sulphur-containing organic compound, characterised in that the inhibitor of crust formation is chosen from amongst the anions derived from arylsulphonic acids.
COMPLETE SPECIFICATION
(ORIGINAL)

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

APPLICANT'S REF.: S.76/53

Name(s) of Applicant(s): SOLVAY & CIE.

Address(es) of Applicant(s): 33 rue du Prince Albert, B-1050 Brussels, Belgium.

Actual Inventor(s): DANIEL TYTGAT, STEPHANE NOEL and LUCIEN CLERBOIS.

Address for Service is: PHILLIPS, ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
37-41 Queen Street
Melbourne, Australia, 3000

Complete Specification for the invention entitled:
"PROCESS FOR THE POLYMERISATION, IN AQUEOUS SUSPENSION, OF HALOGEN-CONTAINING VINYL MONOMERS"

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):
The present invention relates to a process for the polymerisation, in aqueous suspension, of halogen-containing vinyl monomers.

Polymerisation in aqueous suspension is a polymerisation technique which is currently used in the manufacture of polymers based on halogen-containing vinyl monomers. It consists in polymerising the said monomers in the form of droplets which are dispersed in water by means of mechanical stirring and in the presence of dispersing agents, using polymerisation initiators which are liposoluble and generate free radicals. Polymerisation in aqueous suspension is generally carried out in accordance with a discontinuous process in reactors, possessing a steel kettle, provided with a paddle stirrer and, optionally, baffles. Solid deposits of polymers, generally called "crusts", which adhere strongly to the internal surfaces of the reactors,(kettles, stirrers and baffles),are usually formed during the polymerisation. This phenomenon is generally referred to by the name of crust formation.

Crust formation is extremely disadvantageous. In fact, the crusts covering the interior of the kettle reduce the amount of heat which it is possible to remove by means of the heat transfer fluid circulating in the double jacket with which the reactors are generally provided. As a result, the productivity is reduced because it is necessary to use lower speeds of polymerisation than if there was no crust formation.

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Furthermore, it frequently happens that during polymerisation the crusts detach partially and contaminate the polymers obtained, which then contain infusible nodules originating from the crusts and commonly referred to as "fish-eyes".

Finally, crust formation, which always takes place irregularly, makes it more difficult to carry out, and control, the polymerisation cycles.

Admittedly, it is customary to clean the internal surfaces of the reactors after each polymerisation cycle. This cleaning is frequently carried out manually, but there are also more complex techniques which employ hot solvents or devices which spray jets of water at high velocity. However, this cleaning is always a laborious operation which is expensive in manual work, power and material, and which immobilises the polymerisation reactor for a long time.

It is for this reason that attempts have been made to prevent crust formation from taking place, by adding, to the polymerisation mixture, various additives having an inhibiting effect on crust formation. Thus, in Belgian Patent 837,056 filed on 24.12.1975 in the name of SHINETSU CHEM CO, it is proposed to treat the walls of the reactors, which are intended to be used for the polymerisation of vinyl chloride, with a) at least one polar organic compound such as, for example, a sulphur-containing organic compound, and b) at least one compound chosen from amongst the halides, hydroxides, oxides and
carboxylates of the metallic elements belonging to periods 2 to 6 of groups IIB and III to VII of the periodic table, and the oxo-acids derived from the same elements. Furthermore, a solution or dispersion of the compounds a) and/or b) is added to the polymerisation mixture in order to improve the effectiveness of the treatment. For the treatment of the walls to reduce the formation of crusts effectively, it is moreover essential to bring the compounds a) and b) into contact with each other at a temperature of at least 50°C. In order to do this, the solutions or dispersions of these compounds are heated prior to their application to the walls, or the said solutions or dispersions are applied in the cold and the coated walls are heated thereafter. In all cases, the prior treatment of the walls constitutes an operation which detracts from the productivity of the polymerisation installations. In addition, the treatment is generally not totally effective.

The Applicant Company has now found a simple and effective process for reducing crust formation in the reactors used for the polymerisation, in aqueous suspension, of halogen-containing vinyl monomers. This process results from the selection of a class of polar organic compounds, and more particularly of a class of sulphur-containing organic compounds, which are totally effective without the necessity of applying them whilst hot to the walls of the polymerisation reactors or of using them in combination with compounds derived from
metals.

Accordingly, the present invention relates to a process for the polymerisation, in aqueous suspension, of halogen-containing vinyl monomers, using liposoluble initiators which generate free radicals, in the presence of an effective amount of an inhibitor of crust formation derived from a sulphur-containing organic compound, in which process the inhibitor of crust formation is chosen from amongst the anions derived from arylsulphonic acids.

The anions used as inhibitors of crust formation in accordance with the present invention can be derived from any sulphonic acid which contains, in its molecule, at least one sulphonic group -SO₂⁻H directly bonded to a carbon atom which forms part of a hydrocarbon aromatic nucleus. Arylsulphonic acid is therefore to be understood as denoting arylmonosulphonic acids as well as arylidi- and arylpolysulphonic acids. Nevertheless, anions derived from arylmonosulphonic acids and from aryldisulphonic acids, and even more particularly those derived from arylmonosulphonic acids, are preferably used.

Furthermore, it does not matter whether the aryl radical of the arylsulphonic acids is derived from a monocyclic aromatic hydrocarbon, which may or may not be substituted, or from a polycyclic aromatic hydrocarbon, which may or may not be substituted and may or may not contain fused rings. In the case where the aryl radical is derived from a substituted aromatic hydrocarbon, the best results are obtained with substituents chosen, on the one hand,
from amongst alkyl, cycloalkyl and thiol groupings, and even more particularly alkyl groupings containing from 1 to 4 carbon atoms, and, on the other hand, from amongst amino and anilino groupings, and even more particularly amino and aminoanilino groupings corresponding to the general formula

\[ \text{NH} \]

\[ \text{H}_2 \text{N} \]

Examples of anions which can be used according to the present invention are those derived from benzene-sulphonic, trichlorobenzenesulphonic, mono-, di and tri-aminobenzenesulphonic, anilinobenzenesulphonic, aminoanilinobenzenesulphonic, aminoanilinoaminobenzenesulphonic, toluenesulphonic, xylenesulphonic, mesitylenesulphonic, (tert.-butyl)-benzenesulphonic, bis(tert.-butyl)-benzenesulphonic, tris-(tert.-butyl)-benzenesulphonic, biphenylsulphonic, biphenyldisulphonic, naphthalenesulphonic and naphthalenedisulphonic acids.

The most efficient of all the anions which can be used according to the present invention are those derived, on the one hand, from arylsulphonic acids, the aryl radical of which is derived from an aromatic hydrocarbon, which may or may not be substituted, comprising at least two fused rings and, on the other hand, from arylsulphonic acids, the aryl radical of which is derived from a monocyclic aromatic hydrocarbon substituted by the groupings defined above.

Anions which are very particularly preferred are
those which are derived, on the one hand, from naphthalene-
sulphonic acids, and more particularly from alpha-naphthalene-
sulphonic acid, and on the other hand, from xylene sulphonic
acids, and more particularly from para-xylene sulphonic acid,
and from aminoanilinoaminobenzenesulphonic acids, and more
particularly from 2-(p-aminoanilino)-5-aminobenzenesulphonic
acid. This acid corresponds to the general formula

\[
\text{H}_2\text{N} - \text{NH} - \text{SO}_3\text{H}
\]

The anions can be employed in the process according to
the present invention in the form of any compound which
is water-soluble and which dissociates in water to form
the anions defined above. In particular, the anions
can be generated from the corresponding aryl sulfonic
acids and their salts. Amongst these, the alkaline
earth metal salts and even more the alkali metal salts, for
example the potassium and sodium salts, are preferred.
The inhibitor of crust formation is advantageously used in
the form of alkali metal salts of the corresponding aryl-
sulphonic acids, and even more particularly in the form
of sodium salts.

The process according to the invention is applicable
to the polymerisation of halogen-containing vinyl monomers.
The term halogen-containing vinyl monomers is intended to
denote all the monomers, polymerisable by radical poly-
merisation, which possess terminal olefinic unsaturation
and are substituted by at least one halogen. Preferably, these monomers are chosen from amongst the substituted derivatives of ethylene and only contain two carbon atoms. By way of examples of such monomers there may be mentioned vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene fluoride, chlorotrifluoroethylene and tetrafluoroethylene. The invention is preferably applied to the polymerisation of fluorine-containing and chlorine-containing vinyl monomers. It is particularly suitable for polymerising chlorine-containing vinyl monomers and very especially vinyl chloride.

The term polymerisation is intended to denote both the homopolymerisation of the halogen-containing vinyl monomers and their copolymerisation with one another or with other monomers copolymerisable with them. By way of examples of the latter there may be mentioned the vinyl esters such as vinyl acetate, the acrylic esters such as methyl acrylate and glycidyl methacrylate, the unsaturated nitriles such as acrylonitrile and methacrylonitrile, the unsaturated diesters such as dibutyl maleate, the allyl esters such as allyl acetate, the unsaturated amides such as acrylamide, the derivatives of styrene and the \(\alpha\)-olefines such as ethylene and propylene.

However, the invention is preferably applied to the manufacture of polymers containing, in their molecule, at least 50 mol %, and more particularly at least 80 mol %, of units derived from halogen-containing vinyl monomers.

The invention is applicable both to the manufacture
of statistical copolymers and to the manufacture of block or graft copolymers.

Polymerisation of the halogen-containing vinyl monomers is carried out in the presence of the customary ingredients for polymerisation in aqueous suspension, namely in the presence of suspending agents or dispersing agents and of oil-soluble initiators which generate free radicals. Conventional dispersing agents are generally used, such as finely dispersed solids, gelatines, water-soluble cellulosic ethers, synthetic polymers such as polyvinyl alcohols, polyvinylpyrrolidone and vinyl acetate-maleic anhydride copolymers, and their mixtures. It is also possible to employ surface-active agents at the same time as the dispersing agents. The amount of dispersing agent employed generally varies between 0.5 and 1.5% by weight relative to the water.

Any lipo-soluble initiator can be used in the suspension polymerisation according to the invention. By way of examples, there may be mentioned the peroxides such as di-tertiary butyl peroxide, lauroyl peroxide and acetyl-cyclohexylsulphonym peroxide, the azo compounds such as azo-bis-isobutyrionitrile and azo-bis-2,4-dimethylvaleronitrile, the dialkyl peroxydicarbonates such as diethyl, diisopropyl, dicyclohexyl and di-tertiary butyl-cyclohexyl peroxydicarbonates, and the alkyl-boron compounds. In general, these initiators are employed at a rate of 0.01 to 1% by weight relative to the monomers.

In addition to the dispersing agents and initiators,
the polymerisation mixture can also contain various additives normally employed in the conventional technique for polymerisation in aqueous suspension. By way of examples of such additives there may be mentioned buffers, agents for regulating the diameter of the polymer particles, molecular weight regulators, stabilisers, plasticisers and dyestuffs as well as reinforcing agents or agents which facilitate the processing of the polymers.

The operating conditions for the polymerisation process according to the invention do not differ from those usually employed. Thus, in the case of the polymerisation of vinyl chloride, the temperature is in general between 35 and $80^\circ$C. The absolute pressure is in general less than 15 kg/cm$^2$. The pH is in general acid, for example between 2 and 7. The amount of water employed is in general such that the total weight of the monomers represents 20 to 50% of the total weight of the water and the monomers.

In general, the polymerisation of the halogen-containing vinyl monomers is carried out discontinuously in cycles in which water is first introduced, followed by the various components of the reaction mixture (dispersing agents, initiators, monomers, and the like). According to a preferred embodiment of the invention, the inhibitor of crust formation is introduced into the polymerisation mixture before any halogen-containing vinyl monomer, the best results being obtained if it is introduced also before any initiators. To do this, it suffices to add the inhibitor of crust formation after the water has been introduced.
optionally at the same time as the dispersing agents.

It is also possible to introduce the inhibitor of crust formation into the polymerisation mixture in several stages during the polymerisation, or continuously.

To cause the polymerisation to start, the polymerisation mixture is heated, for example by means of the heat transfer fluid circulating inside the double jacket with which the reactors are usually provided. Preferably, the inhibitor of crust formation is introduced into the polymerisation mixture before starting the heating.

If the polymerisation is carried out continuously, the inhibitor of crust formation is preferably also introduced continuously into the polymerisation mixture.

The amounts of inhibitor of crust formation to be employed can vary very widely especially depending on the nature of the monomers and on the condition of the internal surfaces of the reactors used. In general, an amount of inhibitor of crust formation such that the polymerisation mixture contains at least 0.1 ppm thereof, relative to the water, is used. Preferably, the polymerisation mixture contains at least 1 ppm of inhibitor relative to the water. The best results are obtained if the polymerisation mixture contains at least 5 ppm of inhibitor of crust formation, relative to the water.

There is no disadvantage in using large amounts of the inhibitor of crust formation. However, it is in general pointless to exceed a content, in the polymerisation mixture, of 10,000 ppm of inhibitor of crust formation,
relative to the water. Most frequently, a content of at most 1,000 ppm suffices. In virtually all the cases, a content equal to at most 100 ppm is entirely satisfactory. Usually, a content of at most 50 ppm is not exceeded.

According to a preferred embodiment of the invention, from about 5 to 50 ppm, and even more particularly from about 5 to 25 ppm, of inhibitor of crust formation are used, relative to the water present in the polymerisation mixture.

It has been observed that a certain amount of inhibitor of crust formation is adsorbed on the internal metallic surfaces of the polymerisation reactors. For this reason it is preferred that the polymerisation mixture should contain an amount of inhibitor of crust formation at least equal to 1 mg per square metre of internal metallic surface area, and preferably at least 5 mg/m$^2$.

Also for this reason, a certain amount of inhibitor of crust formation can remain adsorbed on the internal metallic surfaces of the reactors at the end of a polymerisation cycle, and exert its effects during the next cycle. It is possible to take this quantity into account and reduce the amount added during the next cycle.

When starting to use the process according to the invention in a particular reactor, it is of value first to clean the internal surfaces particularly carefully. To do this, it is possible to employ particularly efficient solvents for the polymers which form the crusts, to carry out a pyrolysis of the walls, or to carry out descaling or even repolishing.
The inhibitors of crust formation which form the subject of the present invention are remarkably effective, and their use does not demand any prior treatment of the internal walls of the reactors. They are already completely effective when about 7 ppm relative to the water are used. Furthermore, they include a very large number of compounds which do not exhibit any adverse secondary effect as regards the appearance of the polymer, its colour, its odour, its heat and light stability and its ability to be used in foodstuff packaging.

The polymers obtained according to the present invention can be used for all the customary applications of this type of product and especially for the manufacture of articles such as bottles or profiles in accordance with the conventional techniques of, for example, extrusion-blowing and extrusion.

The examples which follow are intended to illustrate the invention and in no way limit it.

**Examples 1 to 5**

Examples 1, 2, 3 and 4 are carried out according to the invention. Example 5 (R) is given by way of comparison.

A stainless steel laboratory reactor of 3 litres capacity, equipped with a double jacket in which a heat transfer fluid flows and with a conventional paddle stirrer made of stainless steel, is used. The internal surfaces of the reactor are cleaned by washing by means of tetrahydrofurane, followed by pyrolysis carried out by heating
the wall to 400°C for 30 minutes. The reactor is then descaled by means of a hydrofluoric acid/nitric acid bath, after which it is rinsed 5 times with demineralised water.

1,500 g of demineralised water and 10 mg of the sodium salt of a sulphonie acid (Examples 1, 2, 3 and 5 (R)), or 10 mg of a sulphonie acid (Example 4), respectively are introduced successively into the reactor. Thereafter, 1.65 g of polyvinyl alcohol are introduced. The stirrer is started. Thereafter, the reactor is twice subjected to a vacuum (of 100 mm of mercury, absolute pressure) and between the two operations the reactor is flushed with technical-grade nitrogen at an absolute pressure of 1,360 mm of mercury. 1,000 g of vinyl chloride and then 500 mg of diethyl peroxodicarbonate are introduced. The polymerisation mixture is heated to 61°C at the rate of 1°C per minute.

The polymerisation mixture is kept at 61°C whilst stirring until the absolute pressure drops by 3.5 kg/cm². The polymerisation is then stopped by letting down the pressure in the reactor and vaporising the unpolymerised vinyl chloride. The mixture is cooled and the polymer is collected by filtration followed by drying.

Table I below specifies the nature of the inhibitor of crust formation used, as well as the result of the inspection of the internal surfaces of the reactor at the end of the polymerisation cycle.

- 14 -
<table>
<thead>
<tr>
<th>Example No.</th>
<th>Inhibitor of crust formation</th>
<th>Result of the inspection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-xylene sulphonate</td>
<td>No soiling of the walls</td>
</tr>
<tr>
<td>2</td>
<td>α-naphthalene sulphonate</td>
<td>No soiling of the walls</td>
</tr>
<tr>
<td>3</td>
<td>trichlorobenzene-sulphonate</td>
<td>Slight soiling; the walls are coated with a thin continuous film</td>
</tr>
<tr>
<td>4</td>
<td>2-(p-aminoanilino)-5-aminobenzene sulphonate</td>
<td>No soiling of the walls</td>
</tr>
<tr>
<td>5 (R)</td>
<td>dioctylsulphosuccinate</td>
<td>Significant soiling; the walls are coated with a thick and sticky deposit.</td>
</tr>
</tbody>
</table>

These examples demonstrate the superiority of the anions derived from arylsulphonic acids, and more particularly that of the anions derived from p-xylene sulphonic, alpha-naphthalene sulphonic and 2-(p-aminoanilino)-5-aminobenzene sulphonic acids over sulphur-containing organic compounds, and even more particularly over non-aromatic sulphonic acids.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for the polymerisation, in aqueous suspension, of halogen-containing vinyl monomers, using lipo-soluble initiators which generate free radicals, in the presence of an effective amount of an inhibitor of crust formation derived from a sulphur-containing organic compound, characterised in that the inhibitor of crust formation is chosen from amongst the anions derived from arylsulphonic acids.

2. Process according to Claim 1, characterised in that the anions are derived from an arylmonosulphonic acid.

3. Process according to Claim 1, characterised in that the anions are derived from an aryldisulphonic acid.

4. Process according to any one of Claims 1 to 3, characterised in that the aryl radical of the arylsulphonic acid is derived from a monocyclic aromatic hydrocarbon substituted by groupings chosen from amongst alkyl, cycloalkyl and thiol groupings.

5. Process according to Claim 4, characterised in that the substituent groupings are chosen from amongst alkyl groupings containing from 1 to 4 carbon atoms.

6. Process according to any one of Claims 1, 2 and 4, characterised in that the anions are derived from para-xylenesulphonic acid.

7. Process according to any one of Claims 1 to 3, characterised in that the aryl radical of the arylsulphonic acid is derived from a monocyclic aromatic hydrocarbon substituted by groupings chosen from amongst amino and...
anilino groupings.

8. Process according to Claim 7, characterised in that the substituent anilino groupings are chosen from amongst the aminoanilino groupings.

9. Process according to any one of Claims 1, 2 and 7, characterised in that the anions are derived from 2-(p-aminoanilino)-5-aminobenzenesulphonic acid.

10. Process according to any one of Claims 1 to 3, characterised in that the aryl radical of the arylsulphonic acid is derived from an aromatic hydrocarbon comprising at least two fused rings.

11. Process according to any one of Claims 1, 2 and 10, characterised in that the anions are derived from alphannaphthalenesulphonic acid.

12. Process according to any one of Claims 1 to 11, characterised in that the anions are introduced into the polymerisation mixture in the form of alkali metal salts of the corresponding arylsulphonic acids.

13. Process according to any one of Claims 1 to 11, characterised in that the anions are introduced into the polymerisation mixture in the form of the corresponding arylsulphonic acid.

14. Process according to any one of Claims 1 to 13, characterised in that the anions are introduced into the polymerisation mixture before the halogen-containing vinyl monomers.

15. Process according to any one of Claims 1 to 14, characterised in that the anions are introduced into the
polymerisation mixture before the oil-soluble initiators which generate free radicals.

16. Process according to any one of Claims 1 to 15, characterised in that the anions are used at a rate of at least 1 ppm relative to the water present in the polymerisation mixture.

17. Process according to Claim 16, characterised in that the anions are used at a rate of at least 5 ppm relative to the water present in the polymerisation mixture.

18. Process according to any one of Claims 1 to 17, characterised in that the anions are used at a rate of less than 100 ppm relative to the water present in the polymerisation mixture.

19. Process according to Claim 18, characterised in that the anions are used at a rate of less than 50 ppm relative to the water present in the polymerisation mixture.

20. Process according to any one of Claims 1 to 19, characterised in that the anions are used at a rate of at least 5 mg per square metre of internal metallic surface area of the reactors.

21. Process according to any one of Claims 1 to 20, characterised in that the anions are introduced into the polymerisation mixture before the latter is heated to cause the polymerisation reaction to start.

22. Process according to any one of Claims 1 to 21, characterised in that it is applied to the polymerisation of halogen-containing vinyl monomers chosen from amongst the fluorine-containing and chlorine-containing monomers.
derived from ethylene.

23. Process according to Claim 22, characterised in that it is applied to the polymerisation of vinyl chloride.

24. Process according to any one of Claims 1 to 23, characterised in that it is applied to the manufacture of polymers containing at least 80 mol % of units derived from halogen-containing vinyl monomers.


PHILLIPS ORMONDE AND FITZPATRICK,
Attorneys for:
SOLVAY & CIE.

[Signature]