



(86) Date de dépôt PCT/PCT Filing Date: 1996/05/31  
 (87) Date publication PCT/PCT Publication Date: 1996/12/12  
 (45) Date de délivrance/Issue Date: 2002/08/06  
 (85) Entrée phase nationale/National Entry: 1997/12/03  
 (86) N° demande PCT/PCT Application No.: IT 1996/000112  
 (87) N° publication PCT/PCT Publication No.: 1996/039446  
 (30) Priorité/Priority: 1995/06/05 (UD95A000109) IT

(51) Cl.Int.<sup>6</sup>/Int.Cl.<sup>6</sup> C08F 2/00, C08F 2/16  
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(54) Titre : PROCEDE DE POLYMERISATION AVEC DES AGENTS ANTI-ECAILLAGE  
 (54) Title: POLYMERIZATION PROCESS WITH ANTI-SCALING AGENTS

(57) **Abrégé/Abstract:**

Procedure for the polymerization of monomers in aqueous suspension and/or emulsion carried out in reactors inside of which an anti-scaling product is deposited, characterized in that, the said anti-scaling product comes from the cross-linking of polyvinyl alcohol with the product formed by the reaction of sodium salt of the hydroxymethansulphinal acid with naphthols.

**ABSTRACT**

1           Procedure for the polymerization of monomers in  
2           aqueous suspension and/or emulsion carried out in reactors  
3           inside of which an anti-scaling product is deposited,  
4           characterized in that, the said anti-scaling product comes  
5           from the cross-linking of polyvinyl alcohol with the  
6           product formed by the reaction of sodium salt of the  
7           hydroxymethansulphincal acid with naphthols.

DESCRIPTION

Polymerarization Process with anti-scaling agents

Technical Field

The object of this invention is a polymerization process with anti-scaling agent for polymerizing of monomers in suspension or aqueous emulsion carried out in reactors (vessel/s) inside the walls of which an anti-scaling agent coating has been deposited capable of eliminating any scale formation or polymer film, and a process that leads to a composition of colourless and effective coating for the entire duration of the polymerization reaction.

Anti-scaling agents for polymerizing reactors and their application techniques are already well known in prior art.

Background Art

At the present state of the art there are also different types of anti-scalers, (by anti-scaler or anti-scalers, anti-scaling agent/s is intended) for each type of polymer and for each of these there are different methods of application to form an anti-scaling coating on the inside of the reactors themselves.

For example the anti-scaler and its application technique for the polymerization of the vinyl chloride is not the same as that used in the reactor for the production of polystyrene or for the production of acrylic polymers, and so on.

This fact necessitates in the storing of various products, spraying and application devices with all the consequences of high management costs.

Disclosure of Invention

A first aim of this invention is to make an anti-scaler and a simple application technique that operates well in any type of

1 polymerizing reactor and for the most varied types of different  
2 materials, therefore for polystyrene as well as for acrylic polymers,  
3 ABS, polyurethane and Polyvinylchloride, etc.

4 In the specific case of polymerization in aqueous suspension  
5 and of polymerization in aqueous emulsion of the vinyl chloride for  
6 example, it is known that in the reactors, a substantial deposit of scale  
7 forms having as main drawbacks:

8 - a consistent maintenance for removing the scale with consequent  
9 interruption of the production, opening of the reactor and therefore  
10 high quantities of gaseous vinyl monomer chloride (VCM) emissions  
11 into the atmosphere;

12 - pollution of the resultant product as some of the scaling parts go  
13 into the respective polymerized product with consequent worsening  
14 in quality and complaints by the users;

15 - in conclusion there are obstacles both in the productive system and  
16 in ecological problems for the areas in which the industrial  
17 Polyvinylchloride plants (P.V.C.) operates.

18 This problem practically exists for all types of polymerizations.

19 Furthermore the anti-scaling products (agents) destined to coat  
20 the surfaces of the respective reactors are of a bluish colour or dark  
21 brown nearly black, wherefore the particles that detach from the  
22 crust, pollute the obtained polymer (for example obtained polyvinyl  
23 chloride) from the reactor under the form of black dots, that for  
24 example in the finished products worsens the qualitative aspect of the  
25 said product.

26 Furthermore it is to be noted that the material particles that  
27 detach from the crust of the reactor wall, end up in the product in  
28 reaction, constituting the pollution of the same, dealing generally

1 with toxic products.

2 In prior art, the technique of condensation or  
3 polycondensation of naphthols and phenol with an aldehydic cross-  
4 linking product (e.g. formaldehyde and others), to obtain anti-scaling  
5 products is known.

6 For this purpose one refers to:

7 • US-A-3669946 (filed in the U.S. on August 31st, 1970, disclosed  
8 on June 13th, 1972), that suggests the use of formaldehyde and ketonic  
9 composites, naphthol etc. and also alpha-naphthylamine and  
10 nigrosin. This teaching predivulges the general concept of forming  
11 anti-scalers condensate parting from the formaldehyde with phenols  
12 and naphthols derivatives.

13 • U.S.-A-3825434 (23rd July 1974) describes an anti-scaling  
14 agent for the polymerizing of vinyl chloride, obtained from the  
15 condensation of the phenol with formaldehyde, where obviously for  
16 definition in this patent the obtained product is always classified as  
17 pertinent to the phenol-formaldehyde or polyarylphenol family.

18 • US-4,068,059 (filed on 17-2-77; published on the 10-1-78)  
19 explains furthermore the importance of using as anti-scalers,  
20 products that in their chemical structure contain one or more of the  
21 following groups: -OH; -COOH; SO<sub>3</sub>H and SO<sub>3</sub>Na.

22 These groups are usually attached to an aromatic nucleus.

23 • EP-A-0052421 describes a process for obtaining an anti-  
24 scaling product formed with formaldehyde that is made to react with  
25 1-naphthol (alpha-naphthol), in which both the nuclear positions 2  
26 and 4 are not replaced and the nuclear position 3 is not replaced or  
27 has a substitute that is not strongly eletron-attractor to obtain a  
28 condensate.

1 Even in this case the product obtained according to the  
2 chemistry is to be considered always as pertinent to the  
3 polyarylphenol family.

4 JP-A-5-230 112 refers to a condensation product based on an  
5 aromatic amine and aromatic hydroxy compounds and are prepared  
6 with use of reaction terminators.

7 In particular it is suggested to use a MeOH solution of 4-  
8 aminodiphenylamine and 2,7-dihydroxynaphthalene heated in the  
9 presence of p-benzoquinone (catalyst) for a certain period, combined  
10 with an aqueous solution of Rongalite<sup>\*</sup> and stirred for a certain period  
11 to give a condensation product.

12 These latter products have the drawback to supply, a dark  
13 brown or dark blue nearly black product, and not always being  
14 suitable for usages in sectors of polymerizing with different  
15 materials.

16 In particular the last one is worse than the previous ones  
17 because Rongalite is used to terminate the reaction to give a  
18 condensation product. The condensation product being one of the  
19 causes giving said dark brown or dark blue nearly black product,  
20 because the condensate particles are of a visible size and produce in  
21 the suspension a dark - bluish colour.

22 Obviously this dark bluish colour gives to the resulting polymerized  
23 product a visible contamination.

24 With these anti-scaling agents the reaction to product  
25 polymers eg. polyvinyl chloride, is difficult to control and leads to  
26 reticulate products insoluble in alkaline aqueous solution.

27 Furthermore, the coating of the reactor with these anti-scalers  
28 is consumed easily dispersing itself in the material in reaction,

\* Denotes Trade Mark

1 polluting it by colour and by toxicity.

2 Furthermore we must point out that these anti-scalers are of  
3 poor efficacy, or however require a massive deposit of scale on the  
4 wall, such to preclude some usages, as for example, sanitary and  
5 alimentary, where the requested limits of polluting products in the  
6 finished product are decidedly lower etc..

7 To obtain a good anti-scale efficacy, they must however deposit  
8 on the wall in high quantities which also affects costs.

9 The colour of the anti-scalers of the known technique is dark  
10 and little appreciated by the user also because it makes one think of a  
11 pollutant product.

12 The dark colour of the product leads to a crust on the wall, also  
13 of dark colour (blackish) and this does not allow to see eventual  
14 application defects. But much more serious is that already mentioned,  
15 that during the reaction crust particles detach and mix with the  
16 polymer. As these crust parts are black it is clear that there is a  
17 qualitative worsening of the product.

18 It is thought that these anti-scaling coatings, even if additives  
19 of partially hydrolysed polyvinyl acetates of other binders and  
20 sprayers with nitrogen or aqueous vapour on the inside of the  
21 polymerization reactors, form colloidal films not attached to the  
22 metallic structure of the walls with electronic ties. In conclusion  
23 these films, dried and placed in the interface between the mass in  
24 polymerization and the surface of the reactor itself when they are  
25 subjected to abrasion phenomena due to solid particles of polymers in  
26 aqueous suspension subjected to rotational agitation, in a short time  
27 detach from the reactor walls.

28 Aim of the present invention is that to obviate the above-

1 mentioned drawbacks and in particular to obviate the dark colour of  
2 the product and to the poor adherence of the coating that it will form  
3 on the wall of the reactor.

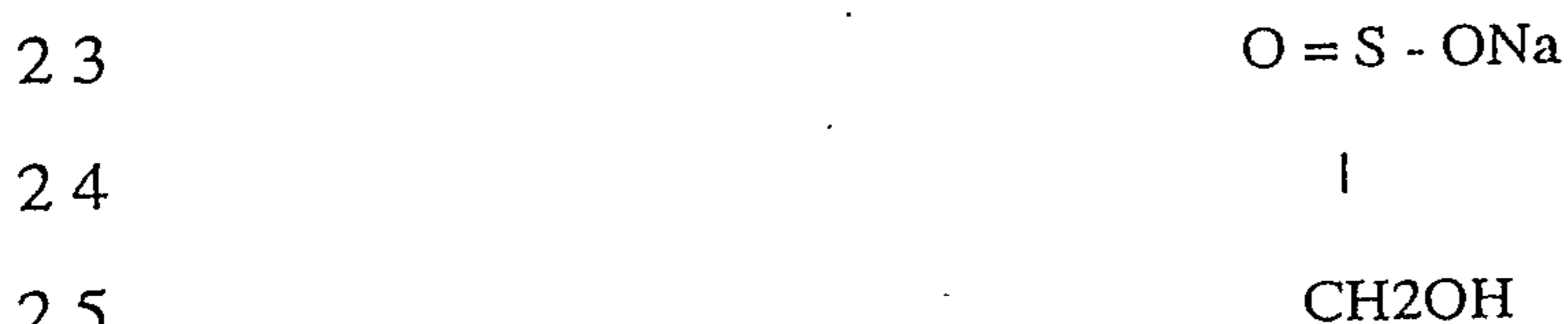
4 The inventors originally thought of making an anti-scaling  
5 product that once applied onto the wall of the reactor is substantially  
6 colourless and strongly adherent to the metallic surfaces of the  
7 reactor itself.

8 It is known that for whitening an aromatic product, for  
9 example colorants, hydrosulphite sodium or hydrosulphite potassium  
10 is used.

11 Attempts to make colourless with hydrosulphite the condensate  
12 of formaldehyde and 1-naphthol have given negative results because  
13 the condensate result always remained bluish black tending to form  
14 deposits even if conducted in absence of oxygen, example presence of  
15 nitrogen.

16 In proceeding the research it was thought to avoid the reaction  
17 between formaldehyde and 1-naphthol in order to substitute it with a  
18 less toxic substance and able to form a colourless product.

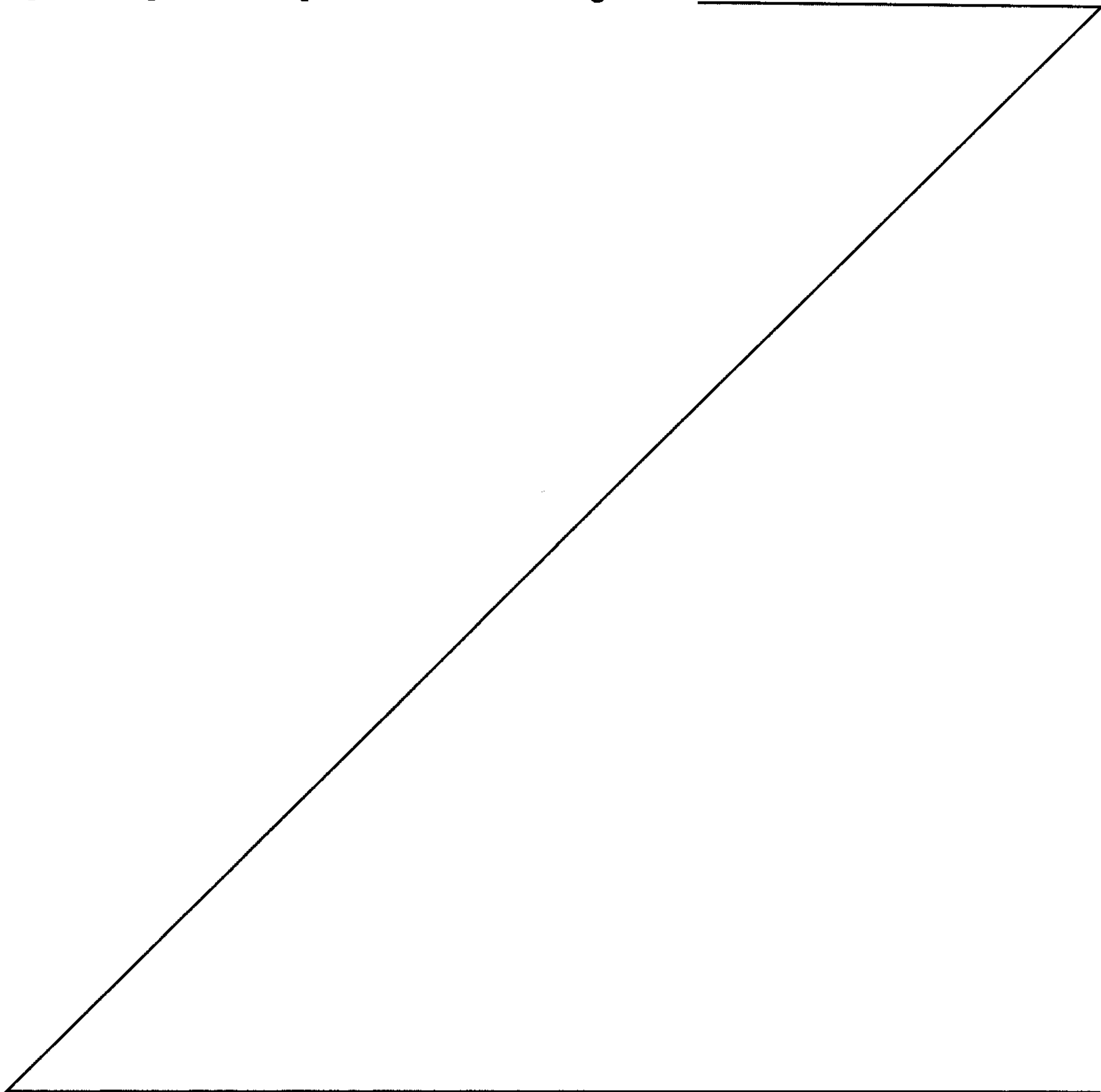
19 After innumerable experimentations it was found that the best  
20 result can be obtained by combining the 1-naphthol with  
21 hydroxymethansulphinal acid (sodium hydroxymethansulphinate)  
22 with the following formula:



23  
24  
25  
26  
27  
28 The product obtained was perfectly colourless.

## 6(a)

1           In a broad aspect, therefore, the present invention relates to a process for the  
2 preparation and application of an anti-scaling coating for the walls of a polymerization  
3 vessel by reacting aromatic hydroxy compounds with sodium hydroxymethansulphinate,  
4 comprising: (i) first reacting sodium hydroxymethansulphinate with 1-naphthol in a basic  
5 environment having a pH value of 11-13 to prevent the evolution of the reaction into  
6 stable condensate forms; (ii) maintaining the resulting liquid mixture in the absence of  
7 oxygen; (iii) adding to said resulting liquid mixture polyvinyl alcohols having a degree  
8 of hydrolysis higher than 99% OH and molecular weight between 70,000 and 90,000 to  
9 obtain a final product; (iv) applying said final product to the internal walls of a said  
10 polymerization vessel, maintained at about 85°C, by means of mixing and injection with  
11 aqueous vapour with a pressure of about 10 Kg./cm<sup>2</sup>.



1 Using the hydroxymethansulphinal acid mixed with the 1-  
2 naphthol in the weight proportions of 1 to 1,5, in an aqueous solution  
3 of 10 to 40%, and bringing the temperature of the solution between  
4 70° and 95°C in a nitrogen atmosphere, alkaline environment (pH 11-  
5 13), a clear transparent coloured product is obtained, fully reaching  
6 the prefixed aim and without decreasing the quality of the product,  
7 infact improving it.

8 The product results physically of clear aspect, transparent, but  
9 if left in the presence of air for a certain period it oxidizes slightly  
10 verging towards a green blue colour.

11 If the contact with oxygen is interrupted, the product reverts to  
12 its original transparent clear aspect.

13 This physical behaviour proves that one has reached a  
14 completely new and structurally different product if compared to the  
15 products of prior art, where this physical phenomenon could not be  
16 observed.

17 If is thought that the reversibility of the phenomenon could be  
18 tied to the presence of a radical in the product, that depending on the  
19 concentrations of oxygen it may or may not be tied to the molecular  
20 structure of the primary compound.

21 In conclusion according to the more probable deductions it  
22 should deal with an abducted bisulphitic of the first product that  
23 forms in the reaction between 1-naphthol and  
24 hydroxymethansulphinal acid.

25 The product applied onto the surface of the reactor in an  
26 atmosphere deprived of oxygen, after drying, results an opalescent  
27 white opaque colour, contrarily to the dark colour of the present anti-  
28 scalers.

1 It is also known that to make the polyvinyl alcohols less soluble  
2 in water and able to form a very resistant film, cross-linking  
3 reactions between the hydroxyl groups of the polyvinyl alcohol and  
4 substances containing radicals able to inter-act with the hydroxyl  
5 groups themselves should be encouraged in the polymerization  
6 reaction.

7 Therefore we had the idea to apply this technique adding to the  
8 previously described colourless product, polyvinyl alcohol's having a  
9 degree of hydrolysis higher than 99% OH and the molecular weight  
10 between 70.000 and 90.000 and to apply this mixture to the internal  
11 walls of the reactor, maintained at about 85°C, by means of mixing and  
12 injection with aqueous vapour with a pressure of about 10 Kg./cm<sup>2</sup>.

13 The results were surprisingly good.

14 Advantageously it was discovered that the coating inside the  
15 reactors was colourless, very uniform and resistant to rubbing.

16 Spraying the product with water vapour at high temperature  
17 the maximum adherence result is obtained.

18 As the reaction of polymerizing in reactor lasts on average  
19 from four to six hours it is evident that in this time and in absence of  
20 oxygen, there are no substantial degradations of the product, and  
21 consequently colorimetric degradations, therefore once the reaction  
22 of polymerizing is completed and once the smallest anti-scaling  
23 percent is integrated in the polymerized mass, this will not undergo  
24 further important contaminations and degradations.

25 Instead, whilst in prior art using the anti-scaling products  
26 previously known, one had to fully wash and empty the reactor of  
27 every minimum trace of the residue of the product applied onto the  
28 wall as an anti-scaler, with this new product, it is possible to send the

1 rinse of the reactor to the tank collection of the aqueous suspensions  
2 of the polymer obtained without requiring further refuse discharges,  
3 realizing in this way a complete and effective and above all economic  
4 technology of the loading and unloading of reactors of polymerization  
5 with the technique named by the experts of the sector as man hole  
6 closed.

7 As the hydroxymethansulphinal acid may be also used with a  
8 molar hydrosulphite excess, even using this product a condensate of  
9 analogous or improved performance (largely reducing conditions) is  
10 obtained.

11 As both in this case and that of the preceding, the activity of  
12 the product is always given from the presence of bisulphate  
13 derivatives and in particular of radical bisulphites present in the  
14 derivative, this characteristic clearly distinguishes the new product  
15 from the prior art, and in particular with reference to the resulting  
16 structure of the derived product, this identifies as innovator for the  
17 presence of an interposed carbon atom between the aromatic rings  
18 and tied to a sulphonic group.

19 This bisulphitic product inhibited from sodium salt of  
20 hydroxymethansulphinal acid is perfectly able to cross-link  
21 polyvinyl alcohol present and therefore form strongly resistant  
22 reticulated combinations with the metals of the walls of the  
23 reactors(Iron, Nickel, Chrome).

24 Hydroxymethansulphinal acid is also found in trade under the name  
25 rhongalite.\*

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\* Denotes Trade Mark

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation and application of an anti-scaling coating for the walls of a polymerization vessel by reacting aromatic hydroxy compounds with sodium hydroxymethansulphinate, comprising:
  - i) first reacting sodium hydroxymethansulphinate with 1-naphthol in a basic environment having a pH value of 11-13 to prevent the evolution of the reaction into stable condensate forms;
  - ii) maintaining the resulting liquid mixture in the absence of oxygen;
  - iii) adding to said resulting liquid mixture polyvinyl alcohols having a degree of hydrolysis higher than 99% OH and molecular weight between 70,000 and 90,000 to obtain a final product;
  - iv) applying said final product to the internal walls of a said polymerization vessel, maintained at about 85°C, by means of mixing and injection with aqueous vapour with a pressure of about 10 Kg./cm<sup>2</sup>.
2. An anti-scaling coating obtained by the process of claim 1.
3. An anti-scaling coating applied on the walls of a said polymerization vessel according to claim 1, characterized in that it contains bisulphitic radicals.
4. An anti-scaling coating on the walls of said polymerization vessel according to claim 1, characterized in that it contains hydrosulphite.