

SPECIFICATION

APPARATUS AND PROCESS FOR THE POLYMERIZATION OF VINYL CHLORIDE MONOMERS

5 The present invention relates to apparatus for the polymerization of monomer comprising vinyl chloride and to a polymerization process using such apparatus. The invention is applicable both to the homopolymerization of vinyl chloride and to the copolymerization of a mixture comprising vinyl chloride as the main component and a monomer copolymerizable with vinyl chloride. 5

In the production of vinyl chloride polymers on an industrial scale, the polymerization vessels used have either been glass-lined or lined with or made of austenitic stainless steel (Cr/Ni stainless steel). 10 Glass-lined polymerization vessels, however, have a number of disadvantages (specifically, that the glass layer is so weak that it can easily be damaged by mechanical or thermal shock and that the heat transfer coefficient, which determines production capacity, is small) which cancel out the advantages (specifically, weak adhesion of scale to the vessel and high resistance to chlorine ion corrosion) of glass-lined vessels. On the other hand, austenitic stainless steel polymerization vessels are superior to glass-lined ones in that they have a large heat transfer coefficient, but they have the disadvantages that 15 resistance to corrosion and pitting corrosion by chlorine ions generated during the polymerization is low, a large quantity of scale is attached to the walls of the vessel as a result of the corrosion and pitting corrosion, and adhesion between the scale and the vessel is firm. 15

Formation of scale on the inside walls of polymerization vessels reduces the heat transfer ability, which, in turn, reduces the production capacity, causes a reduction in the efficiency of the 20 polymerization cycle (as a result of the need to remove the scale) and increases the cost of the process because the scale has to be removed. Consequently, it is desirable to avoid the formation of scale. 20

We have now discovered that the formation of scale can be substantially or completely prevented and corrosion by chlorine ions can be minimized, during a vinyl chloride polymerization process, by 25 using a lining comprising ferritic stainless steel or a duplex phase stainless steel comprising a ferritic phase and an austenitic phase as a lining for those parts where scale formation and corrosion should be minimized and by polishing such a lining to a mirror finish. Clearly, it is not necessary that the whole of the polymerization vessel should be made out of such ferritic or duplex phase stainless steels and the lining can be limited to only some of those parts of or attached to the polymerization vessel which come 30 into contact with the polymerization medium. 30

Thus, the present invention consists in apparatus for the polymerization of monomer comprising vinyl chloride, said apparatus comprising a polymerization vessel in which the inside wall and/or the surface of attachments to the vessel coming into contact with said monomer is made wholly or partially of ferritic stainless steel (containing from 15 to 40% by weight of chromium, from 0.5 to 5% by weight of molybdenum, not more than 0.5% by weight of nickel, not more than 0.05% by weight of carbon and not 35 more than 0.05% by weight of nitrogen) or of duplex phase stainless steel (comprising a ferritic phase and an austenitic phase) said stainless steel having a mirror surface having a gloss of at least 70% [according to Method 2 of Japanese Industrial Standard (JIS) Z—8741 (1962)]. 35

The invention further consists in a process for the production of a vinyl chloride polymer in which 40 monomer comprising vinyl chloride is polymerized in the apparatus of the invention, preferably under radical polymerization conditions in the presence of a radical-generating catalyst, and in an aqueous medium. 40

The ferritic stainless steel which may be used in the apparatus of the invention has a chromium content of from 15 to 40% by weight, and preferably from 17 to 35% by weight. If a stainless steel having 45 a chromium content less than 15% by weight is employed, the resistance to chlorine ion corrosion is too low for practical purposes. On the other hand, if the chromium content exceeds 40% by weight, the cost of the material is too high for economic industrial use. The molybdenum content of this ferritic stainless steel is from 0.5 to 5% by weight, and preferably from 1 to 3% by weight. If the molybdenum content is 50 less than 0.5% by weight, the improvement in corrosion resistance resulting from the interaction between molybdenum and chromium is inadequate; on the other hand, when the content exceeds 5% by weight, the further improvement in corrosion resistance is not substantial but the cost of the material is greatly increased. The ferritic stainless steel should have a nickel content not more than 0.5% by weight, and preferably not more than 0.3% by weight, since a nickel content exceeding 0.5% by weight produces a steel having much reduced resistance to stress corrosion cracking. Also, the ferritic stainless steel 55 should have nitrogen and carbon contents each not exceeding 0.05% by weight, and preferably not exceeding 0.02% by weight, since the steel will otherwise have substantially reduced corrosion resistance, processability and weldability. 55

In addition to the elements specifically mentioned above, ferritic stainless steel may, as is well-known in the art, contain other elements (either as incidental impurities or as deliberate additives), 60 possibly in amounts up to several percent. For example, it matters little if the ferritic stainless steel contains no more than several percent of titanium and/or niobium and/or zirconium or similar metals, which are commonly added to stabilize ferritic stainless steel. The balance of the steel, of course, consists of iron. 60

The duplex phase stainless steel (otherwise known as ferrite : austenite series stainless steel) which is an alternative material for use in the apparatus of the invention preferably contains from 17 to 30% by weight of chromium and from 2 to 8% by weight of nickel. In addition to these elements, this stainless steel may contain any one or more of molybdenum, zirconium, copper, tungsten or similar metals, which are conventionally added in order to improve corrosion resistance and/or in order to stabilize the structure. The strength of the duplex phase stainless steel may be improved by the incorporation of a small quantity of nitrogen. The balance of the steel, of course, consists of iron.

Apart from using ferritic or duplex phase stainless steel, it is also an essential feature of the invention that the surfaces made of these materials should be polished to a mirror finish. In this Specification, the measure of mirror gloss is carried out according to Method 2 of JIS Z—8741(1962), in which a mirror coated with vacuum-evaporated silver is taken as a standard having a gloss of 100%. The internal walls or other surfaces composed of the ferritic or duplex phase stainless steel should have a mirror gloss of at least 70%, and preferably at least 75%. With such a mirror gloss, scale formation can more completely be prevented.

Mirror polishing of the stainless steel to obtain the desired surface finish can be achieved by a number of methods well-known to those skilled in the art. For example, the surface can be mechanically ground with a buff (grade No. 400 or more) and then mirror-polished with abrasives for stainless steel, such as polishing rods. Alternatively, the surface can be mechanically ground with a buff (grade No. 300 or more) and then mirror-polished by electropolishing. Another alternative is to mirror-polish by simultaneous mechanical buffing and electroplating. Buff grades 300 and 400 refer to the particle size of the abrasive particles: with buff grade 300, the abrasive particles pass a 300 mesh standard sieve; with buff grade 400, the abrasive particles pass a 400 mesh standard sieve.

In a series of experiments, test pieces having a mirror gloss of 70% or more obtained by mirror polishing ferritic or duplex phase stainless steel in accordance with the present invention showed no formation of scale and significantly improved resistance to corrosion during the polymerization of monomer comprising vinyl chloride.

Common austenitic stainless steel, although generally corrosion resistant, is subject to pitting corrosion during the polymerization of vinyl chloride as a result of the action of chlorine ions, even if the steel is mirror polished. This pitting corrosion causes and further promotes scale formation. On the other hand, under normal conditions of use, ferritic stainless steel and duplex phase stainless steel are considered to be much superior to austenitic stainless steel in their resistance to stress corrosion cracking, but they are inferior or equal to austenitic stainless steel in their resistance to pitting corrosion and resistance to crevice corrosion. Contrary to expectation, however, we have found that ferritic stainless steel and duplex phase stainless steel, when mirror polished, give rise to substantially no formation of scale and have a much improved corrosion resistance.

Although we do not wish to be limited by any theory, it is considered probable that the high level of mirror polishing applied to the ferritic stainless steel or duplex phase stainless steel forms on the surface of the steel a dense and firm, especially passive, film, which prevents the formation of scale and gives rise to a higher corrosion resistance than otherwise expected.

The advantages of the corrosion resistance of mirror-polished ferritic or duplex phase stainless steel during the polymerization of vinyl chloride can be exploited in a number of ways. For example, all of the major structures of the polymerization vessel can be made out of such polished ferritic or duplex phase stainless steel. Alternatively, all of the major structures of the polymerization vessel may be made out of mild or high-tensile steel and then the required ferritic stainless steel or duplex phase stainless steel is strip-lined (clad) or explosion-lined (clad) on to the mild or high tensile steel to form the inner wall of the vessel. A further alternative is to form the vessel from clad steel, which is made by sticking the ferritic or duplex phase stainless steel onto the surface of mild steel by explosion-lining or roll-lining. The particular method adopted will be selected taking into account the size of the polymerization vessel and economy.

The advantages of the present invention are achieved to a maximum during the radical polymerization of monomer comprising vinyl chloride in an aqueous medium, that is to say in suspension polymerization or in emulsion polymerization. The same advantages are also to be expected in bulk polymerization or solution polymerization using a small amount of water.

In suspension polymerization, oil-soluble catalysts and suspension stabilizers, such as are commonly employed in the suspension polymerization of vinyl chloride, may be used. Examples of suitable oil-soluble catalysts include diacyl peroxides (e.g. lauroyl peroxide), alkyl peroxyesters (e.g. t-butyl peroxy-pivalate), dialkyl peroxydicarbonates (e.g. diisopropyl peroxydicarbonate), acetyl alkyl peroxides (e.g. acetyl cyclohexyl sulphonylperoxide), azo catalysts [e.g. azobis(2,4-dimethyl-valeronitrile)] and mixtures of any two or more thereof. However, the present invention is not limited to the use of such catalysts. Any amount of catalyst commonly used in suspension polymerization may be employed, although we generally prefer to use from 0.005 to 0.5% by weight of catalyst, based on the weight of monomer. Suitable suspension stabilizers include water-soluble synthetic high molecular weight polymers (e.g. partially saponified polyvinyl alcohol), cellulose derivatives (e.g. hydroxy-propoxymethyl cellulose) and natural high molecular weight polymers (e.g. gelatin).

In emulsion polymerization, water-soluble catalysts and emulsifiers of a type commonly used in

emulsion polymerization of vinyl chloride may be employed. Suitable water-soluble catalysts include persulphates (e.g. potassium persulphate), hydrogen peroxide and redox catalysts, which may be produced from a reducing agent and a persulphate or hydrogen peroxide. Suitable emulsifiers include anionic surface active agents, such as alkali metal salts of alkylsulphuric acids (e.g. sodium lauryl-

5 sulphate) and alkali metal salts of alkylarylsulphonic acids (e.g. sodium dodecylbenzene sulphonate). The polymerization is generally carried out at a temperature from 40°C to 80°C and, in some cases, a chain transfer agent or a cross-linking agent may be added. 5

The process of the invention may be employed for the homopolymerization of vinyl chloride or for the copolymerization of vinyl chloride with a suitable copolymerizable monomer. Examples of 10 copolymerizable monomers include: α -olefins (e.g. ethylene or propylene), halogenated vinyl compounds other than vinyl chloride, halogenated vinylidene compounds (e.g. vinylidene chloride), vinyl ethers (e.g. methyl vinyl ether or lauryl vinyl ether) and vinyl esters (e.g. vinyl acetate). 10

By using the apparatus of the invention, the formation of scale which would otherwise accompany the polymerization of vinyl chloride can be prevented substantially or completely. Thus cleaning of the 15 inside walls of polymerization vessels, which is carried out after each polymerization cycle, becomes very easy. For example, it is generally possible to clean the inside walls merely using a jet of low pressure water (50 kg/cm² or less). 15

The invention is further illustrated by the following Examples.

EXAMPLE 1.

20 On the lower part of a baffle (a part completely soaked in the reaction medium during polymerization) in a 20 cubic metre glass-lined polymerization vessel for the production of vinyl chloride polymers were mounted test pieces of thickness 2 mm and size 100 × 100 mm. The composition and degree of surface polishing of each of the test pieces are shown in Table 1 and the chemical composition of the stainless steels of which they were made is shown in Table 2. 20

25 To the polymerization vessel were then added 10,000 kg of deionized water, 5.6 kg of polyvinyl alcohol (average degree of polymerization 850, degree of saponification 75%) and 2.8 kg of a toluene solution containing 50% by weight of diisopropyl peroxydicarbonate. After deaerating the vessel, 7,000 kg of vinyl chloride were added, and this was then 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 had dropped, 30 after 7 hours, by 2 kg/cm², the polymerization was terminated and unreacted vinyl chloride monomer was recovered. The contents were then withdrawn from the vessel and the vessel was washed with low pressure water at 15 kg/cm² gauge. 30

Cycles composed of the above-described operation (taking, on average, about 12 hours per cycle) were repeated for about 6 months, thereby producing 360 batches of polymer. During that period, the 35 test pieces were detached at the times shown in Table 1 and evaluated for the degree of scale attachment and of corrosion and then re-mounted, at which point the test was continued. 35

TABLE 1

Test piece No.	Material	State of surface-finishing		After first cycle Scale (2) attachment (g/m ²)
		Method	Mirror (1) gloss (%)	
1	YUS-190	Polishing with a buff #400 followed by electro-polishing	87	0
2	E-Brite 26-1	Same as above	84	0
3	SHOMAC	Same as above	86	0
4	YUS-190	Polishing with a buff #400 followed by mirror-polishing	79	0
5	E-Brite 26-1	Same as above	78	0
6	SHOMAC	Same as above	76	0
7	YUS-190	Polishing alone with a buff #300	62	21
8	E-Brite 26-1	Same as above	65	48
9	SHOMAC	Same as above	65	45
10	YUS 304	Polishing with a buff #400 followed by electro-polishing	82	38
11	YUS 316	Same as above	84	21
12	YUS 316L	Same as above	85	15
13	YUS 434	Same as above	83	52

TABLE 1 (Continued)

After 60th cycle		After 360th cycle		
Scale(2) attachment (g/m ²)	Corrosion state (g/m ² hr)	Scale(2) attachment (g/m ²)	Corrosion state	
			(g/m ² hr)	Surface state
0	0.001	0	0.001	Sound
0	0.001	0	0.001	Sound
0	0.002	0	0.003	Sound
0	0.001	0	0.002	Sound
0	0.002	0	0.002	Sound
0	0.003	0	0.005	Sound
43	0.009	130	0.105	Many pits
63	0.007	96	0.079	Many pits
50	0.007	115	0.090	Many pits
67	0.015	270	0.316	Many pits
46	0.008	130	0.120	Many pits
45	0.007	95	0.065	Many pits
91	0.023	230	0.203	Many pits

Note:

- (1) Mirror gloss is measured according to the method No. 2 of JIS Z-8741 (1962) (the gloss of a mirror coated with vacuum-evaporated silver is taken as 100%).
- (2) Values after washing with low-pressure water at 15 kg/cm gauge.

TABLE 2
Chemical composition of stainless steel

Trade Name	Chemical component (weight %)					
	Cr	Mo	Ni	C	N	Others
YUS 190	19.0	2.1	0.12	0.008	0.009	Ti 0.15 Nb 0.27
E-Brite 26-1	26.0	1.0	0.12	0.001	0.01	
SHOMAC	30.0	2.0	0.18	0.003	0.007	
YUS 434	16.5	1.0	—	0.12	0.2	
YUS 304	19.1	—	8.5	0.08	0.1	Mn 1.5
YUS 316	16.9	2.5	10	0.07	0.1	Mn 1.7
YUS 316L	16.8	2.5	10	0.02	0.1	

The stainless steels sold by the trade names YUS 190, E-Brite 26—1 and SHOMAC are manufactured by Shin-Nippon Seitetsu Company, Aircro Company, (USA) and Showa Denko Company, respectively, and are all ferritic stainless steels in accordance with the present invention. Steels YUS 434, YUS 304, YUS 316 and YUS 316L are all manufactured by Shin-Nippon Seitetsu Company and YUS 434 is a ferritic stainless steel outside the scope of the present invention, whilst the others are austenitic stainless steels.

From the data shown in Table 1, it can be seen that test pieces Nos. 1 to 6, in which the materials and the degree of surface finishing are in accordance with the present invention, do not show substantial scale formation not only in the short term but also over a long period of time and, moreover, they show only a very slight progress of corrosion. On the other hand, test pieces Nos. 7 to 9, which are made of ferritic stainless steel in accordance with the requirements of the present invention but which have a poor surface finish, and test pieces Nos. 10 to 13, which are made of stainless steels other than those specified in the present invention, show firm scale formation (which means that the scale could not be removed by washing with low pressure water at 15 kg/cm² gauge) and rapid progress of corrosion and these conditions became worse as the test period grew longer.

EXAMPLE 2.

The whole of the inside wall of a 100 litre SUS 316L polymerization vessel was strip-lined with a thin plate (0.5 mm thick) made of YUS 190, whose chemical composition is shown in Table 2, and then the surface of the wall was given a sufficiently smooth finish by mechanical polishing. The wall was then electropolished at 70°C and a current density of 50 A/dm², using an electrolytic bath containing 45% by weight phosphoric acid, 35% by weight sulphuric acid and 3% by weight chromic acid. The average mirror gloss of five representative points on the inside wall was 81%, confirming that the inside wall had a high level of mirror polishing.

Into this 100 litre vessel were charged 45 kg of deionized water, 30 g of polyvinyl alcohol (having an average degree of polymerization of 850 and an average degree of saponification of 75 mole %) and 12 g of a toluene solution containing 50% by weight of diisopropyl peroxydicarbonate. After deaerating the vessel, 30 kg of vinyl chloride monomer were added and then polymerized, with stirring, at 57°C. At the beginning of the polymerization, the pressure in the vessel was 8.7 kg/cm² gauge. When the pressure had dropped by 2 kg/cm², which took place after 7 hours, the polymerization was terminated and unreacted vinyl chloride monomer was recovered. The contents of the vessel were then withdrawn and the vessel was washed with low pressure water at 15 kg/cm² gauge. On washing with this low pressure water, polymer particles loosely attached to the inside wall were removed very easily and completely.

The above cycle of operations (taking on average about 12 hours per cycle) was repeated for 10 days, thus producing 20 batches of polymer. No attachment of polymer particles and no scale were observed even after the twentieth cycle. On detailed observation of the surface, no corrosion (such as pitting corrosion) was observed and the surface was seen to be sound.

EXAMPLE 3.

After the experiment described in Example 2, comprising repeated suspension polymerization, had finished, an emulsion polymerization process was carried out in the same vessel.

Into the 100 litre vessel were charged 45 kg of deionized water, 24 g of potassium persulphate and 80 g sodium laurylsulphate. After deaeration and replacement of the air in the vessel by nitrogen, 34 kg of vinyl chloride monomer were added, and this was then polymerized, with stirring, at 53°C. The polymerization was stopped when the pressure in the vessel dropped by 1 kg/cm², and then the vinyl chloride monomer was recovered and the contents of the vessel were withdrawn. The product was a vinyl chloride polymer latex having an average particle size of 0.4 μ . A thin film-like scale was seen to be attached to the inside wall of the vessel after withdrawing the contents, but this was completely removed by washing with low pressure water at 30 kg/cm² gauge.

Cycles of these operations (taking, on average, about 12 hours per cycle) were repeated for 10 days to produce 20 batches of polymer. Even after completion of the twentieth cycle, no accumulation of scale was observed and the original gloss was still maintained. Detailed observation confirmed that there was no corrosion (such as pitting corrosion or crevice corrosion) and that the surface had kept sound.

COMPARATIVE EXAMPLE 1.

Vinyl chloride was suspension polymerized under the same conditions as in Example 1, using a 100 litre SUS 316L polymerization vessel, the surface of the inside wall of which had been finished with a buff grade No. 300 to a mirror gloss of 63%. When the polymerization had finished, the inside wall was washed with a jet of water at 100 kg/cm² gauge, but it was impossible to remove completely the scale, which was thin but firmly attached to the wall. The remaining scale was scratched from the wall and then weighed; it weighed 160 g.

COMPARATIVE EXAMPLE 2.

Vinyl chloride was emulsion polymerized under the same conditions as in Example 3, using the same vessel as in Comparative Example 1. When the polymerization was complete the inside wall of the vessel was washed with a jet of water at 100 kg/cm² gauge. It was, however, almost impossible to remove the scale which was thin but very firmly attached to the wall. The remaining scale was detached from the wall by scratching, and was then weighed. It weighed 330 g.

EXAMPLE 4.

On the lower part of a baffle (a part completely soaked in the reaction medium during polymerization) in a 22 cubic metre glass-lined polymerization vessel of a type commonly used for the production of vinyl chloride polymers were mounted test pieces of size 100 x 100 mm and thickness 2 mm. The composition and degree of surface finishing of each of the test pieces are shown in Table 3 and the chemical composition of the stainless steel used is shown in Table 4.

Into the polymerization vessel were charged 10,000 kg of deionized water, 5.6 kg of polyvinyl alcohol (average degree of polymerization 850, degree of saponification 75%) and 2.8 kg of a toluene solution containing 50% by weight of diisopropyl peroxydicarbonate. After deaeration of the vessel, 7,000 kg of vinyl chloride monomer were added, and this was then 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 had dropped by 2 kg/cm², which occurred after 7 hours, the polymerization was terminated and unreacted vinyl chloride monomer was recovered. The contents of the vessel were then withdrawn and the vessel was washed with low pressure water at 15 kg/cm² gauge.

Cycles comprising the above operations, each cycle lasting on average, about 12 hours, were repeated for about 6 months to produce 360 batches of polymer. During that period, the test pieces were removed at the times shown in Table 3 and examined to determine the degree of scale attachment and corrosion, before being remounted and continuing the test.

TABLE 3

Test piece No.	Material	State of surface-finishing		After first cycle Scale(2) attachment (g/m ²)
		Method	Mirror(1) gloss (%)	
1	NAR-F	Polishing with a buff #400 followed by electropolishing	81	0
2	NTK R-4	Same as above	83	0
3	NAS 45-M	Same as above	77	0
4	Sandvik* 3RE60	Same as above	79	0
5	NAR-F	Polishing alone with a buff #300	61	11
6	NAS 45-M	Same as above	63	7
7	YUS 304	Polishing with a buff #400 followed by electropolishing	82	38
8	YUS 316	Same as above	84	21
9	YUS 316L	Same as above	85	15

* Registered Trade Mark

Note:

- (1) Mirror gloss is measured according to the method No. 2 of JIS Z 8741 (1962) (the gloss of a mirror coated with vacuum-evaporated silver is taken as 100%).
- (2) Values after washing with low-pressure water of 15 kg/cm²G.

TABLE 3 (Continued)

After 60th cycle		After 360th cycle		
Scale (2) attachment (g/m ²)	Corrosion state (g/m ² hr)	Scale (2) attachment (g/m ²)	Corrosion state	
			(g/m ² hr)	Surface state
0	0.001	0	0.002	Sound
0	0.002	0	0.003	Sound
0	0.003	0	0.003	Sound
0	0.003	0	0.003	Sound
25	0.005	47	0.085	Many pits
17	0.007	30	0.035	Many pits
67	0.015	270	0.316	Many pits
46	0.008	130	0.120	Many pits
45	0.007	95	0.065	Many pits

TABLE 4

Chemical composition of stainless steel

Material	Chemical component (weight %)					
	C	Cr	Ni	Mo	Cu	Others
NAR—F	0.02	25.1	5.1	1.6		
NTK R—4	0.02	24.7	4.5	1.5		Ti: 0.2
NAS 45—M	0.02	24.0	5.0	1.5	1.5	
Sandvik 3RE60	0.01	18.5	4.7	2.7		Si: 1.7
YUS 304	0.08	19.1	8.5	—		Mn: 1.5
YUS 316	0.07	16.9	10	2.5		Mn: 1.5
YUS 316L	0.02	16.8	10	2.5		

NAR—F, NTK R—4, NAS 45—M and Sandvik 3RE60 are all duplex phase stainless steels, manufactured by Nippon Stainless Co., Nippon Kinzoku Kogyo Co., Nippon Yakin Kogyo Co. and Sandvikens Co. (Sweden), respectively. YUS 304, YUS 316 and YUS 316L are all austenitic stainless steels made by Shin-nippon Seitetsu Co. (Japan).

From the results shown in Table 3, it can be seen that there is no substantial scale attachment and only very slight corrosion at all stages of the process on test pieces 1 to 4, in which the composition and degree of surface finishing are in accordance with the present invention. On the other hand, with test pieces 5 and 6 (which are made of a duplex phase stainless steel, as required by the present invention, but which have a poor degree of surface finishing), and test pieces 7, 8 and 9 (which are made of stainless steels having a composition other than that required by the present invention), there is firm scale attachment (which means that scale is not removable by washing with low pressure water at 15 kg/cm² gauge) and rapid progress of corrosion and these conditions become worse as the test progresses.

EXAMPLE 5.

The whole of the inside wall of a 100 litre polymerization vessel made of SUS 316L was strip-lined with a thin plate (0.5 mm thick) made of NAR—F (whose chemical composition is shown in Table 4) and then this lining was given a sufficiently smooth surface finish by mechanical polishing. The wall was then electro-polished at 70°C and at a current density of 50 A/dm² using an electrolytic bath containing 45% by weight phosphoric acid, 35% sulphuric acid and 3% by chromic acid. The average mirror gloss of five representative points on the inside wall was 80%, indicating a high level of mirror polishing.

Into this 100 litre vessel were charged 45 kg of deionized water, 30 g of polyvinyl alcohol (average degree of polymerization 850, average degree of saponification 75 mole %) and 12 g of a toluene solution containing 50% by weight of diisopropyl peroxydicarbonate. After deaerating the contents of the vessel, 30 kg of vinyl chloride monomer were added, and were then polymerized at 57°C, with stirring. At the beginning of the polymerization, the pressure in the vessel was 8.7 kg/cm² gauge. When the pressure had dropped by 2 kg/cm², which occurred after 7 hours, the polymerization was terminated and unreacted vinyl chloride monomer was recovered. The contents of the vessel were then withdrawn and the vessel was washed with low pressure water at 15 kg/cm² gauge. Washing with this low pressure water easily and completely removed polymer particles loosely attached to the inside wall of the vessel.

The cycle of operations described above took, on average about 12 hours per cycle; the cycle was repeated for 10 days, to produce 20 batches of polymer. Even after the finish of the twentieth cycle, there was no attachment of polymer particles or scale to the wall of the vessel. Detailed examination of the internal surface of the vessel indicated complete absence of corrosion, such as pitting corrosion, and that the surface had kept sound.

EXAMPLE 6.

After the experiment described in Example 5, comprising repeated suspension polymerization, was finished, the same vessel was used for an experiment comprising repeated emulsion polymerization.

Into the 100 litre vessel were charged 45 kg of deionized water, 24 g of potassium persulphate and 80 g of sodium lauryl sulphate. After deaeration and replacement of the air in the vessel by nitrogen, 34

kg of vinyl chloride monomer were added and then polymerized, with stirring, at 53°C. The polymerization was terminated at the time when pressure in the vessel had dropped by 1 kg/cm². Unreacted vinyl chloride monomer was then recovered and the contents of the vessel were withdrawn. The product was a vinyl chloride polymer latex having an average particle size of 0.4 μ . The thin film-like scale attached to the inside wall of the vessel after withdrawal of the contents could be removed completely by washing with low pressure water at 30 kg/cm² gauge.

The cycle comprising the above operations and lasting, on average, 12 hours per cycle was repeated for 10 days to produce 20 batches of polymer. Even after the twentieth cycle was finished, there was no accumulation of scale and the original gloss on the internal wall was maintained. Detailed examination showed the absence of corrosion, such as pitting corrosion and crevice corrosion, and indicated that the surface had kept sound.

COMPARATIVE EXAMPLE 3.

Vinyl chloride was suspension polymerized under the same conditions as are described in Example 4, but using a 100 litre SUS316L polymerization vessel without any internal lining and the surface of whose internal walls had been finished with a 300 grade buff to a mirror gloss of 63%. When the polymerization was complete, the inside wall was washed with a jet of water at 100 kg/cm² gauge. It was, however, impossible completely to remove the scale, which was thin but firmly attached to the wall. The scale remaining after washing was scraped from the wall and weighed; it weighed 160 g.

COMPARATIVE EXAMPLE 4.

Vinyl chloride was emulsion polymerized under the conditions described in Example 6, but using the same vessel as described in Comparative Example 3. When the polymerization was complete, the inside wall of the vessel was washed with a jet of water at 100 kg/cm² gauge. It was, however, almost impossible to remove the scale, which was thin but very firmly attached to the wall. The scale remaining on the wall after washing was scraped off and weighed; it weighed 330 g.

CLAIMS

1. Apparatus for the polymerization of monomer comprising vinyl chloride, said apparatus comprising a polymerization vessel in which the inside wall and/or the surface of attachments to the vessel coming into contact with said monomer is made wholly or partially of ferritic stainless steel (containing from 15 to 40% by weight of chromium, from 0.5 to 5% by weight of molybdenum, not more than 0.5% by weight of nickel, not more than 0.05% by weight of carbon and not more than 0.05% by weight of nitrogen) or of duplex phase stainless steel (comprising a ferritic phase and an austenitic phase) said stainless steel having a mirror surface having a gloss of at least 70% [according to Method 2 of Japanese Industrial Standard Z-8741(1962)].

2. Apparatus according to Claim 1, in which said ferritic stainless steel contains from 17 to 35% by weight of chromium, from 1 to 3% by weight of molybdenum, not more than 0.3% by weight of nickel, not more than 0.02% by weight of carbon and not more than 0.02% by weight of nitrogen.

3. Apparatus according to Claim 1 or Claim 2, in which said mirror gloss is at least 75%.

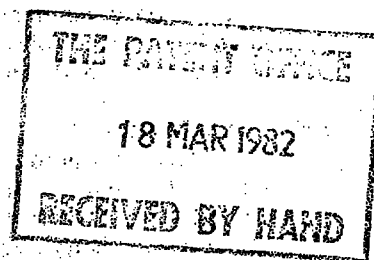
4. Apparatus according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

5. A process for the production of a vinyl chloride polymer, in which monomer comprising vinyl chloride is polymerized in an aqueous medium in apparatus according to any one of the preceding Claims.

6. A process according to Claim 5, in which vinyl chloride is homopolymerized.

7. A process according to Claim 5, substantially as hereinbefore described with reference to any one of the foregoing Examples.

8. A vinyl chloride polymer when produced by a process according to any one of Claims 5, 6 and 7.



(P)



kg of vinyl chloride monomer were added and then polymerized, with stirring, at 53°C. The polymerization was terminated at the time when pressure in the vessel had dropped by 1 kg/cm². Unreacted vinyl chloride monomer was then recovered and the contents of the vessel were withdrawn. The product was a vinyl chloride polymer latex having an average particle size of 0.4 μ . The thin film-like scale attached to the inside wall of the vessel after withdrawal of the contents could be removed completely by washing with low pressure water at 30 kg/cm² gauge.

The cycle comprising the above operations and lasting, on average, 12 hours per cycle was repeated for 10 days to produce 20 batches of polymer. Even after the twentieth cycle was finished, there was no accumulation of scale and the original gloss on the internal wall was maintained. Detailed examination showed the absence of corrosion, such as pitting corrosion and crevice corrosion, and indicated that the surface had kept sound.

COMPARATIVE EXAMPLE 3.

Vinyl chloride was suspension polymerized under the same conditions as are described in Example 4, but using a 100 litre SUS316L polymerization vessel without any internal lining and the surface of whose internal walls had been finished with a 300 grade buff to a mirror gloss of 63%. When the polymerization was complete, the inside wall was washed with a jet of water at 100 kg/cm² gauge. It was, however, impossible completely to remove the scale, which was thin but firmly attached to the wall. The scale remaining after washing was scraped from the wall and weighed; it weighed 160 g.

COMPARATIVE EXAMPLE 4.

Vinyl chloride was emulsion polymerized under the conditions described in Example 6, but using the same vessel as described in Comparative Example 3. When the polymerization was complete, the inside wall of the vessel was washed with a jet of water at 100 kg/cm² gauge. It was, however, almost impossible to remove the scale, which was thin but very firmly attached to the wall. The scale remaining on the wall after washing was scraped off and weighed; it weighed 330 g.

CLAIMS

1. Apparatus for the polymerization of monomer comprising vinyl chloride, said apparatus comprising a polymerization vessel in which the inside wall and/or the surface of attachments to the vessel coming into contact with said monomer is made wholly or partially of ferritic stainless steel (containing from 15 to 40% by weight of chromium, from 0.5 to 5% by weight of molybdenum, not more than 0.5% by weight of nickel, not more than 0.05% by weight of carbon and not more than 0.05% by weight of nitrogen) or of duplex phase stainless steel (comprising a ferritic phase and an austenitic phase) said stainless steel having a mirror surface having a gloss of at least 70% [according to Method 2 of Japanese Industrial Standard Z-8741(1962)].

2. Apparatus according to Claim 1, in which said ferritic stainless steel contains from 17 to 35% by weight of chromium, from 1 to 3% by weight of molybdenum, not more than 0.3% by weight of nickel, not more than 0.02% by weight of carbon and not more than 0.02% by weight of nitrogen.

3. Apparatus according to Claim 1 or Claim 2, in which said mirror gloss is at least 75%.

4. Apparatus according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

5. A process for the production of a vinyl chloride polymer, in which monomer comprising vinyl chloride is polymerized in an aqueous medium in apparatus according to any one of the preceding Claims.

6. A process according to Claim 5, in which vinyl chloride is homopolymerized.

7. A process according to Claim 5, substantially as hereinbefore described with reference to any one of the foregoing Examples.

8. A vinyl chloride polymer when produced by a process according to any one of Claims 5, 6 and 7.

