

Veröffentlichung im Amtsblatt	Ja/Nein
Publication in the Official Journal	Yes/No
Publication au Journal Officiel	Oui/Non

Aktenzeichen / Case Number / N° du recours : T 632/89 - 3.3.3

Anmeldenummer / Filing No / N° de la demande : 80 108 226.4

Veröffentlichungs-Nr. / Publication No / N° de la publication : 0 031 964

Bezeichnung der Erfindung: Sequential emulsion polymerization process for
Title of invention: structured particle latex products
Titre de l'invention :

Klassifikation / Classification / Classement : C08F 263/02

ENTSCHEIDUNG / DECISION

vom / of / du 12 July 1990

Anmelder / Applicant / Demandeur :

Patentinhaber / Proprietor of the patent /
Titulaire du brevet :

The Dow Chemical Company

Einsprechender / Opponent / Opposant :

01 Wacker-Chemie GmbH
02 Röhm GmbH Chemische Fabrik
03 Rhône-Poulenc Chimie de Base

Stichwort / Headword / Référence :

EPU / EPC / CBE Article 56

Schlagwort / Keyword / Mot clé :

"Inventive step (no) - difference in wording
not reflecting a difference in structure"

Leitsatz / Headnote / Sommaire



Case Number : T 632/89 - 3.3.3

DECISION
of the Technical Board of Appeal 3.3.3
of 12 July 1990

Appellant :
(Opponent 03)

Rhône-Poulenc Chimie de Base
25, quai Paul Doumer
F-92408 Courbevoie Cédex
(FR)

Representative :

Fabre, Madeleine-France
Rhône-Poulenc Interservices
Service Brevets Chimie
25, quai Paul Doumer
F-92408 Courbevoie Cédex
(FR)

Other Party :
(Opponent 01)

Wacker-Chemie GmbH
Prinzregentenstrasse 22
Postfach
D-8000 München 22
(DE)

Other Party :
(Opponent 02)

Röhm GmbH Chemische Fabrik
Postfach 4242
D-6100 Darmstadt 1
(DE)

Respondent :
(Proprietor of the patent)

The Dow Chemical Company
P.O. Box 1967
Midland, Michigan 48640
(US)

Representative :

Hann, Michael, Dr.
Patentanwälte Dr. Michael Hann
Dr. H.-G. Sternagel
Sander Aue 30
D-5060 Bergisch Gladbach 2
(DE)

.../...

Decision under appeal : Decision of Opposition Division of the European Patent Office dated 8 August 1989 rejecting the oppositions filed against European patent No. 0 031 964 pursuant to Article 102(2) EPC.

Composition of the Board :

Chairman : F. Antony

Members : C. Gérardin

W. Moser

Summary of Facts and Submissions

- I. The mention of the grant of the patent No. 31 964 in respect of European patent application No. 80 108 226.4 filed on 27 December 1980 and claiming priority of 2 January 1980 of an earlier application in the United States, was published on 5 March 1986 on the basis of 9 claims, Claim 1 reading as follows after a minor clerical amendment ((A(1) changed into (A)(1)):

"A process for preparing an aqueous copolymer latex of colloiddally dispersed, substantially spheroidal, heterogeneous copolymer particles by

- (A) first preparing an initial aqueous latex of a substantially linear hydrophilic polymer by emulsion polymerizing an initial monomer charge comprising (1) one or more vinyl esters of a non-addition polymerizable carboxylic acid and/or one or more esters of an addition polymerizable carboxylic acid and (2) one or more relatively hydrophilic comonomers having a solubility in water of at least 3 weight percent on a total weight basis at 25°C with the proviso that when the monomer component (A)(1) is exclusively vinyl acetate comonomer (2) can be eliminated; and
- (B) thereafter emulsion polymerizing, in the presence of the initial hydrophilic polymer latex of stage (A) a second relatively hydrophobic monomer charge, characterized in that
- (a) in stage (A) the relatively hydrophilic comonomers are used in an amount which renders the copolymer of said initial latex sufficiently hydrophilic that it ultimately becomes preferentially oriented towards the outer

- surface of the finished copolymer particles of the final copolymer latex product,
- (b) the polymerization is performed in both polymerization stages (A) and (B) at a pH from 2 to 6,
 - (c) in polymerization stage (B) from 5 to 50 parts by weight on a polymer solids basis of the initial hydrophilic polymer latex of stage (A) and from 50 to 95 parts by weight of the relatively hydrophobic monomer charge is used,

thus obtaining copolymer particles which are individually composed of a relatively hydrophobic polymer core portion having a relatively hydrophilic polymeric portion preferentially oriented toward the outer surface thereof."

Claims 2 to 8 were directed to preferred embodiments of the process according to the main claim and Claim 9 concerned an aqueous polymer latex prepared by the process according to Claims 1 to 8.

- II. Opponent 01 filed a notice of opposition on 10 September 1986 against the grant of the patent on the grounds of lack of novelty or, in any case, inventive step.

On 20 November 1986 Opponent 02 lodged an opposition to the granted patent and requested revocation thereof on the grounds of lack of novelty and of insufficient disclosure.

On 26 November 1986 the Appellant (Opponent 03) also filed an opposition against the grant of the patent and requested revocation thereof for non-compliance with the various requirements of Article 100 EPC.

These various objections which were emphasized and elaborated in later submissions were based essentially on the following documents:

- (I.2) DE-A-2 811 481
- (III.3) KOBUNSHI RONBUNSU, Eng. Ed., Volume 3, No. 9, 1974, Distribution of Polymers in Particles Produced by New Type Seed-Emulsion Polymerisation, by T. Matsumoto, M. Okubo and T. Imai.

III. The Opposition Division rejected the oppositions in a decision dated 8 August 1989 which was based essentially on the following reasons:

Regarding the objection of insufficient disclosure, reference was made to the arguments provided by the Respondent (Patentee) in the statement filed on 14 September 1988, according to which the specific combination of features giving rise to the phenomenon of inversion, in particular the monomer composition, the sequence of polymerisation steps and the pH conditions, were clearly disclosed in the patent in suit. Since no document mentioned such a combination of features together with an inverted structure, novelty of the claimed subject-matter was acknowledged; this applied particularly to document (I.2), wherein the interaction between the core and the shell polymers resulted in an internal plasticization. As to inventive step, without identifying the closest prior art and without investigating this point following the well-established problem/solution approach, the decision under appeal stated that the neutral and basic pH conditions described in document (I.2) could not suggest the criticality of acid pH conditions in the production of inverted core-shell latexes. Although document (III.3) dealt with the theory behind the alleged

invention, the structures exemplified therein could only be inverted by a modification with more hydrophilic monomers which was not envisaged in this disclosure. The claimed subject-matter was, therefore, inventive.

- IV. The Appellant thereafter filed a notice of appeal by telex on 2 October 1989 and paid the prescribed fee at the same time. The arguments presented in the Statement of Grounds of Appeal filed on 2 December 1989 and in a later submission filed on 21 May 1990 concentrated mainly on an objection of lack of novelty with regard to the disclosure of document (I.2).

It was first argued that the pH values referred to in the impugned decision concerned the conditions for measuring the viscosity and the film forming temperature, not the actual polymerisation conditions which were unambiguously acid in all the examples. Further, the expression "internal plasticization" did not refer to any particular structure, as evidenced by the results of a comparative test showing that latex obtained according to Example 10E of document (I.2) had in fact very similar properties to those mentioned in the description of the patent in suit.

- V. During oral proceedings held on 12 July 1990 the Respondent filed as Main Request a new set of 8 claims, wherein in Claim 1 under (c) the relatively hydrophobic monomer charge (B) was defined as "comprising, based upon the weight thereof, (1) from 20 to 75 weight percent of a monovinylidene monomer selected from monovinylidene aromatic monomers and vinylidene halide monomers, (2) from 25 to 80 weight percent of the aliphatic conjugated diene monomer, and (3) from 0 to 10 weight percent of a monoethylenically unsaturated carboxylic acid." Claims 2 to 8 corresponded to Claims 3 to 9 of the patent as granted.

As an Auxiliary Request, the Respondent filed another set of 7 claims which differed from those submitted as Main Request only by the deletion of Claim 8 (product claim).

VI. Although thereafter the Appellant conceded the novelty of the subject-matter of the so amended Claim 1, he contended that the partial replacement of styrene by an aliphatic conjugated diene monomer, such as butadiene, in the hydrophobic monomer charge was not inventive. In particular, a possible correlation between this compositional feature and the phenomenon of inversion could not be accepted, since the structure of the copolymer according to Example 10E of document (I.2), when examined by electron microscopy, revealed likewise a polystyrene core within the copolymer particle. The only purpose of butadiene was actually to facilitate the inversion; in fact, the selection of this compound was suggested by the above document, since butadiene had the lowest interpenetration parameter which was the prerequisite for inversion.

Furthermore, in view of the paper coating applications aimed at by the Respondent, the copolymerisation of butadiene with styrene was self evident, for polystyrene latexes were well known to be too hard for such use.

VII. In support of the allowability of the claims the Respondent underlined that one should simply stick to the actual wording of document (I.2). The process described there aimed at the preparation of plasticized copolymers by interaction between two polymers, which could not be compared with the phenomenon of inversion between a hydrophilic core seed and a hydrophobic polymer prepared subsequently. As to the choice of butadiene for partially replacing styrene, it was not obvious for two reasons: the first one was that this compound was mentioned among the

monomers of stage (A) only; the second one was that the hydrophobicity of butadiene was too high to expect a relatively weak interaction between the two polymers as required according to the teaching of this document.

VIII. The Appellant requested that the decision under appeal be set aside and that the patent be revoked.

The Respondent requested that the appeal be dismissed and that the patent be maintained on the basis of Claims 1 to 8 of the Main Request or, alternatively, on the basis of Claims 1 to 7 of the Auxiliary Request submitted during the oral proceedings.

Reasons for the Decision

1. The appeal complies with Articles 106 to 108 and Rule 64 EPC and is, therefore, admissible.
2. As mentioned in paragraph III above, the decision under appeal is flawed in that it has not identified the closest prior art, nor has it applied the problem/solution approach when investigating the existence of any inventive step. This could in itself have been a reason for it to be set aside and for the case to be remitted to the first instance in order to complete a proper examination of the oppositions (cf. Decision T 638/88 of 28 May 1990, particularly paragraph 6.2, last two sentences; unpublished). In view of the age of the case (filing date 1980), and because this could not have led, in the Board's opinion, to any different ultimate outcome, the Board has refrained from such remittal and has itself decided the matter.

3. The current wording of the claims does not give rise to any objections under Article 123 EPC.

In substance, the wording of Claim 1 differs from that of Claim 1 as granted or originally filed in that the composition of the relatively hydrophobic monomer charge polymerised in step (B) of the process is specified. These compositional features correspond to Claim 2 as granted, which was in turn based on a combination of Claims 2 and 5 as originally filed. As to Claims 2 to 8, they correspond to respectively Claims 3 to 9 as granted and Claims 3 and 6 to 11 as originally filed with their numbers and, where appropriate, appendancies adjusted.

At the outset, the Board had some doubts whether it should at all consider the new claims submitted during oral proceedings, bearing in mind that these were submitted at a very late stage and were not clearly allowable within the meaning of the decision T 153/85 of 11 December 1986 published in OJ EPO 1988, 1. However, as it was readily apparent that the amendments proposed did not extend beyond the mere combination of two claims and overcame the objection of lack of novelty, as will appear hereinafter, the Board, in exercising its discretionary power, has admitted them with some reluctance.

4. The patent in suit concerns a sequential emulsion polymerisation process for structured particle latex products. Such a process is already known from document (I.2) which the Board regards as the closest state of the art. That document describes a two-step polymerisation process for the preparation of polymer latexes by forming a first polymer by emulsion polymerisation at a pH between 4 and 10 of a first ethylenically unsaturated monomer system comprising comparatively hydrophilic monomers, and

subsequently polymerising in the presence of the resulting hydrophilic polymer a second charge of ethylenically unsaturated monomers which are by themselves the precursors of a harder and more hydrophobic polymer than the first charge polymer (page 10, lines 18 to 26; page 11, lines 2 and 3 in combination with the examples). In principle, any monomer which can be polymerised in the mix and which is itself hydrophilic enough or potentially hydrophilic enough to effectively bind water transmitted into the composition is suitable for the first step (page 11, lines 14 to 17); practical considerations, however based on the ease of polymerisation and the necessity to functionalise the first step polymer, lead to choose a combination of acrylates or methacrylates or esters of vinyl alcohol as major component, together with acrylic or methacrylic acid as minor component (page 12, lines 2 to 18; page 15, lines 1 to 10; page 26, lines 25 to 32). As to the composition of the second step polymer, the only requirements are that the latter should be more hydrophobic and harder than the first polymer, so as to interact to an appropriate degree and thereby achieve internal plasticization of the polymer latex particle (page 17, lines 21 to 29); this interaction merely reflects the compatibility between the first polymer and the monomer charge of the second step (page 22, lines 2 to 9). The description does not specify any compound or group of compounds to be particularly appropriate as second monomer charge, but the only monomers actually exemplified are methyl methacrylate and styrene. In practice, however, the compatibility between the relatively hydrophobic monomer charge and the hydrophilic polymer cannot be regarded as optimal, so that desirable latex characteristics are not attained. Moreover, although these prior art latexes are generally useful for many applications involving forming free films and coatings,

including in paper uses (page 29, last line to page 30, line 11), the polystyrene based latexes tend to be too hard as binder components in paper coating compositions.

In the light of these shortcomings the technical problem underlying the patent in suit can thus be seen in improving the compatibility between the compounds of the two steps as well as reducing the hardness of the polymer latex particles.

This problem is solved according to Claim 1 of the patent in suit by polymerising as relatively hydrophobic monomer charge a mixture which comprises (1) from 20 to 75 weight percent of a monovinylidene monomer selected from monovinylidene aromatic monomers and vinylidene halide monomers, (2) from 25 to 80 weight percent of an aliphatic conjugated diene monomer, and (3) from 0 to 10 weight percent of a monoethylenically unsaturated carboxylic acid.

In view of the examples in the patent in suit, particularly Examples 15 to 23 and Table VI wherein the paper coating evaluations are summarised, the Board is satisfied that the above-defined technical problem has been effectively solved.

5. The Board concurs with the Appellant in that the subject-matter of Claim 1 as granted and as maintained by the decision under appeal, was indeed not novel over the disclosure of document (I.2). However, this assessment needs not be substantiated any further in the present case due to its lack of relevance in the light of the Respondent's present requests (see however point 6.1 hereinbelow).

After examination of all cited documents the Board has reached the conclusion that the subject-matter of present Claim 1 is not disclosed in any of them and that the subject-matter of the patent in suit is, therefore, novel. Since the issue of novelty is no longer raised by the Appellant, it is not necessary to consider this matter in detail.

6. It still remains to be examined whether the subject-matter of the patent in suit involves an inventive step within the meaning of Article 56 EPC with regard to the teaching of the cited documents.
 - 6.1 The first question which arises is whether the structure of the latexes according to document (I.2) which are described as "internally plasticized", on the one hand, and the inverted core-shell structure of the latexes obtained by the process according to the patent in suit, on the other hand, are actually different, i.e. whether this difference in wording really reflects a difference in structure.
 - 6.1.1 The introductory section of the description of document (I.2) explicitly specifies that the sequential polymerisation of a hard, relatively hydrophobic monomer system onto soft, hydrophilic functionalised copolymer latex particles results in latex particles which for convenience (emphasis added by the Board) are called internally plasticized polymer latex particles (page 8, lines 26 to 32). Emphasis is laid on the intrinsic properties of these internally plasticized latexes which are such that for most applications the addition of conventional plasticizers is superfluous (page 29, last line to page 30, line 5). The description further underlines the importance of the fact that the functional (e.g. acid) groups incorporated with the hydrophilic

monomer charge in the first stage of the polymerisation are available for subsequent reaction; this availability distinguishes the internally plasticized polymer latex from a latex in which a second stage so coats or interacts with the first stage as to decrease or eliminate the availability of first stage functional groups for further reactions (page 31, lines 1 to 10). This confers to the internally plasticized polymer latex particles general properties which are unlike the properties of either parent type of polymer, nor are these properties simply the sum or average of the properties of the parents (page 9, lines 31 to 35).

In the Board's view, these various passages only teach that plasticization is not achieved by incorporation of an external plasticizer; in particular, the Board cannot see any relation between the expression "internal plasticization" and a specific structure of the polymer latex particles, inverted or not, as the Respondent argued repeatedly. On the contrary, in the Board's judgment, the necessity for the functional groups of the hydrophilic monomers to be available for subsequent reactions cannot be distinguished from the requirement in the patent in suit according to which these monomers should be oriented towards the outer surface of the copolymer latex particles.

- 6.1.2 In the appeal procedure and particularly during oral proceedings, the Appellant demonstrated that the phenomenon of inversion occurs in the prior art process as well and that the structures of the known internally plasticized copolymer and the inverted core-shell copolymers are in fact identical.

For this purpose, Example 10E on pages 56 to 58 of document (I.2) was repeated (submission filed on 21 May 1990, point 4 and Annex). According to that example, the relatively hydrophilic monomer charge based on vinyl acetate, ethyl acrylate, "vinyl alcohol" and methacrylic acid is polymerised first; the relatively hydrophobic monomer consisting of styrene is then polymerised in the presence of the polymer previously obtained. In the Appellant's test report it is mentioned that the resulting polymer latex particles exhibit all the desirable properties of the inverted core-shell latexes put forward by the Respondent, especially the relatively high film-forming temperature, the presence of acid functions at the surface of the particles determined by potentiometric titration and the influence of the pH under alkaline conditions on the viscosity of these latexes.

During oral proceedings the Appellant additionally submitted the electron micrographs of ruthenium tetraoxide-stained particle cross-sections showing unambiguously that the core phase consists mainly of polystyrene, which necessarily presupposes a core-shell inversion. The validity of this evidence has not been disputed by the Respondent.

- 6.1.3 From the foregoing it follows that the concept of inverted core-shell polymer particles only differs in wording, but not in substance, from the internally plasticized polymer particles described in document (I.2). Therefore, the presence of this concept in the main claim to identify the structure directly obtained by the process presently claimed cannot be regarded as a distinguishing feature over the prior art teaching.

6.2 The issue of inventive step, thus, boils down to the question whether for the skilled person, starting from document (I.2), it was obvious, in the light of the technical problem defined in point 4, second paragraph, above, to partially replace styrene by an aliphatic conjugated diene monomer.

6.2.1 According to document (III.3) the phenomenon of inversion depends directly upon the relative affinity for water of the two polymers in the latex particle. Evidence for this is provided by a first experiment comprising the emulsion polymerisation of ethyl acrylate followed by the polymerisation of styrene using the poly(ethyl acrylate) particles as seeds. The electron micrographs of the emulsion particles reveal that the particles consist of polymer composition distributions having a large amount of polystyrene in the core phase and a large amount of poly(ethyl acrylate) in the shell phase (page 1822, point 3.2.1 to page 1823, line 9). However, when the two steps are carried out in the reverse order, i.e. when ethyl acrylate is seed polymerised in the presence of polystyrene, one still obtains emulsion particles having a polymer distribution with a large amount of polystyrene in the core phase and a large amount of poly(ethyl acrylate) in the shell phase (page 1823, lines 25 to 34). The presence of polystyrene in the core phase in both cases, irrespective of the order of polymerisation, is attributed to the fact that the affinity of polystyrene for water is lower than that of poly(ethyl acrylate) (page 1825, lines 7 to 11).

In a second experiment, by contrast, when styrene is replaced by methyl methacrylate, the seed polymerisation of the latter in the presence of poly(ethyl acrylate) results in a large proportion of poly(methyl methacrylate) in the shell phase; when the order of polymerisation is

altered, i.e. when ethyl acrylate is seed polymerised using poly(methyl methacrylate) as the seed particles, one observes predominantly poly(ethyl acrylate) in the shell phase (page 1825, line 15 to page 1826, line 9). In both cases, thus, the polymer formed by seed polymerisation is confined in the shell phase, which is explained by the similar affinities for water of the two polymers, so that no protrusion phenomenon occurs (page 1827, lines 4 to 6).

The difference in affinity for water between the seed particles and the polymer produced subsequently is thus the essential criterion for inversion; it is self-evident that this difference can be adjusted, i.e. increased to the appropriate level either by making the seed particles more hydrophilic, or the second polymer more hydrophobic.

- 6.2.2 Document (I.2) expresses this criterion in terms of interpenetration parameters and even provides the values thereof which facilitate the choice of polymer-monomer systems which are compatible to ensure the desired interaction.

According to this teaching, to achieve internal plasticization the monomers of the second step must be carefully selected according to the first stage polymer so as to interact to an appropriate degree (page 22, lines 2 to 13). There are both upper and lower limits to the degree of compatibility desired between the first stage polymer and the subsequent monomer charge; the appropriate degree of compatibility is suitably expressed in numerical terms by a property based on solubility parameters and named the interpenetration parameter I_p (pages 24 and 25, Table). As a general rule, the interpenetration parameter of the first stage must be greater than that of the second

stage; however, the desired degree of compatibility can only be achieved if the two parameters differ by at least a certain number of units (page 26, lines 1 to 20).

More specifically, the values mentioned in the above Table enable the identification of the monomers to be incorporated at either stage in order to increase the difference between the two interpenetration parameters and, thereby, according to the technical problem underlying the patent in suit, to improve the compatibility of a styrene based monomer charge ($I_p=12.1$) with an alkyl-acrylate or alkyl-methacrylate or vinyl-acetate based polymer (I_p between 15.0 and 16.2) obtained in the first stage. The first alternative would consist in increasing the first stage value by using additional monomers whose interpenetration parameter is high, such as hydroxy or amino substituted alkyl methacrylate (I_p between 24.2 and 26.2) or by introducing larger amounts of unsaturated carboxylic acid already present (I_p for acrylic acid = 29.2; I_p for methacrylic acid = 28.4). The other option would consist in modifying the second stage charge with monomers having an even lower interpenetration parameter than styrene, such as 1,3-butadiene and isoprene which have the lowest values ($I_p = 9.9$ respectively 10.2); this second method, thus, would point to the use of aliphatic conjugated dienes in combination with styrene. It is significant that both solutions result in a modification of the balance of hydrophobic/hydrophilic character of the two monomer charges in order to control the internal plasticization, which is exactly the conclusion reached in document (III.3).

- 6.2.3 During oral proceedings, the Appellant explained convincingly why practical considerations clearly point to the second of the aforementioned alternatives, i.e. to the use of butadiene together with styrene in the second monomer charge, as follows:

Although document (I.2) mentions a possible use of the internally plasticized polymer latexes in the field of the paper industry (page 30, line 11), the hardness which characterises these prior art latexes (page 28, line 32 to page 29, line 9) is such that they would not be suitable as binder components in paper coating compositions, as envisaged in the patent in suit (Examples 15 to 23). In the Board's view, there is no doubt that the skilled person would not look for a solution to this specific problem by means of increased hydrophilicity or additional functionality of the first stage polymer, as suggested by the first alternative above, but by means of a modification of styrene with butadiene in the second monomer charge according to the second option; for, butadiene and, more generally, conjugated dienes are quite commonly used in latexes as soft monomers in combination with hard monomers, such as styrene, and in practice latexes containing at least 30% butadiene have long supplanted the polystyrene latexes, which are much too hard for this purpose. This critical argument has not been disputed by the Respondent.

- 6.3 In conclusion, for the reasons given above, the subject-matter of Claim 1 according to the Main Request and the Auxiliary Request does not involve an inventive step.

7. Claim 1 not being allowable, the same applies to Claims 2 to 7 according to both sets of claims, which represent preferred embodiments of the subject-matter of the main claims and thus fall with it, and further to Claim 8 according to the Main Request, which is related to an aqueous copolymer latex prepared by the process of Claims 1 to 7 and for the patentability of which no argument has been provided.

Order

For these reasons, it is decided that:

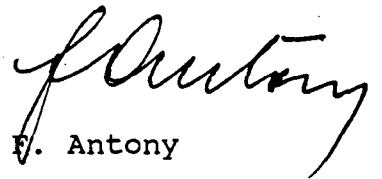
1. The decision under appeal is set aside.
2. The patent is revoked.

The Registrar:



M. Beer

The Chairman:



F. Antony