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(54) Title: REDOX POLYMERISATION COATING PROCESS

(57) Abstract

Coated solids, for example suitable for use as the dispersed phase of an electrorheological fluid, are prepared by effecting polymerisation of at least one coating monomer in the presence of surfaces of a polymer capable itself of acting as the redox initiator for the polymerisation of the monomer.

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REDOX POLYMERISATION COATING PROCESS

This invention relates to coated solids and the preparation and use of such solids and is particularly, but not exclusively, concerned with coated polymers useful as a dispersed phase in the preparation of electrorheological fluids.

Electrorheological fluids are suspensions of a solid dispersed phase in a liquid continuous phase which exhibits an increase in flow resistance on application of an electric field. Research is in continual progress with a view to improving both the dispersed and continuous phases of electrorheological fluids : see, for example, UK Patents Nos. 1501635, 1570234, 2100740, 2119392 and 2153372. However, the mechanisms by which electrorheological phenomena occur are still not fully understood.

Recent developments include the introduction of electrorheological fluids which are capable of functioning electrorheologically when substantially anhydrous as described in UK Patent No. 2170510. The solid phase of such fluids may conveniently be an electronic organic semiconductor such as polyaniline, as described in UK Application Publication No. 2230532A. However, to function satisfactorily in an electrorheological fluid, the polyaniline must be adjusted with base to a form in which it has optimum electrorheological performance, i.e. a form in which the solid has sufficient intrinsic conductivity to allow electronic conduction but where the fluid as a whole does not have undesirably high bulk conductivity.

The present invention seeks to provide for the preparation of improved solids for use as the dispersed phase in electrorheological fluids or for use in other situations where it is desirable to modify the surface properties of materials.

The present invention comprises a polymerisation process initiated by a polymeric redox initiator and the resulting products of such a process. Thus the invention includes a

process for the preparation of a coated solid substrate in which polymerisation of at least one coating monomer is carried out in the presence of surfaces of a polymer capable itself of acting as the redox initiator for the polymerisation of the monomer. The term "polymer" used herein comprises homopolymers and co-polymers.

The invention also includes coated solids prepared by such a process and electrorheological fluids incorporating such solids.

The polymer acting as the redox initiator is suitably a polymer having internal redox capability as exhibited by polyaniline and described, for example, by MacDiarmid et al., Mol. Cryst. Liq. Cryst., 1985, 121, 173-180. Examples of other materials having internal redox capability are polymers of substituted anilines e.g. the toluidines and anisidines, and polymers of diphenylamines and pyrroles. Structures of such typical polymers are illustrated in Figure 1.

The coating monomer may be any vinyl monomer which can be polymerised in solution or suspension in the presence of a redox initiator, such as an alkene monomer, for example styrene or an unsaturated ester monomer such as methyl methacrylate or vinyl acetate. The longer chain alkyl methacrylates containing up to 20 carbon atoms in the alkyl group e.g. lauryl methacrylate provide steric stabilisation of the substrate particles and are therefore preferred. Mixtures of coating monomers may be employed.

The polymer acting as the redox initiator may have any convenient form of surface but is preferably present in particulate form so that the product coated comprises coated particles. It is also contemplated within the scope of the present invention that the redox polymer may be present as a coating on a further material, such as a non-redox initiating polymer e.g., polyethylene or nylon, or an inorganic material such as carbon or glass fibres, so that the polymer acts as a substrate for deposition of a layer of polymerised monomer. It

will be appreciated that, in this way, it is possible to provide a wide range of coated solids in which the properties of the solid are modified by the coating. For example, the intrinsic conductivity of polyaniline can be maintained by provision of a surface coating of, for example, polystyrene, the more insulating nature of which ensures that the bulk conductivity of a dispersion in which such a coated solid is used remains low. Alternatively, the process of the invention may be used to apply an insulating coating to a conductive substrate such as carbon fibres.

It has been surprisingly found that the carrying out of bulk polymerisation or emulsion or solution polymerisation of the monomer in the presence of a polymeric redox initiator results in satisfactory even coating of the polymeric initiator without substantial formation of pure polymerised monomer.

Where bulk polymerisation is employed, the solid redox initiator polymer or composite is added to liquid monomer and after heating to effect polymerisation of the latter the excess monomer is removed. The reaction is therefore a heterogeneous reaction producing a surface effect. This ensures that the polymer is deposited over the surface of the initiating polymer, and in the context of ER fluid formulations, further markedly improves the bulk resistivity of such fluids by electrically insulating the particles. There is some diminution of the mechanical strength in terms of static yield stress if comparisons are made between ER fluids based on coated and uncoated polyanilines or derivatives at identical powder loadings and electrical fields, but the relative drop in current density by using coated material more than compensates for this in terms of lower electrical power dissipation, thereby making superior ER fluids based on these coated powders. From this aspect, the invention may be seen as a process of modifying the surface of an electrorheologically functional polymer characterised in that the polymer is one capable of

acting as a redox initiator of polymerisation and is modified by polymerisation of an olefinically unsaturated monomer at the polymer surface.

The preparation can alternatively be effected in aqueous emulsion, using, if necessary, a suitable surfactant such as Triton X-100 to maintain the emulsion. After completion of polymerisation, the coated solid is then dried to an extent necessary for the intended subsequent use. When preparing a coated solid such as styrene-coated polyaniline for use as the dispersed phase of an electrorheological fluid, it is desirable to obtain as end product a dry non-agglomerated solid capable of good dispersion in the intended continuous phase of the fluid. Suitable continuous phases may be provided by silicone oils, transformer oils or a liquid ester such as diethyl phthalate. Suitable drying techniques include azeotropic drying in the presence of benzene or toluene.

Alternatively, the preparation can be effected in a non-aqueous solvent, such as hexane or heptane. In this case the presence of a surfactant is not required and the drying problems of aqueous systems are obviated. Again, for use in an electrorheological fluid, the coated solid, after filtration, can be dispersed in a suitable continuous phase such as silicone oil or diethyl phthalate. The choice of solvent is determined by the need for a material which is a non-solvent for the polymeric redox initiator and coated product but a solvent or dispersant for the monomer.

The conditions of polymerisation can vary widely dependent on the nature of the polymeric redox initiator and the monomer and on the intended use of the coated solid.

Further co-monomeric materials may be employed to modify the properties of the coating. Variables such as reaction time, temperature and concentration of the starting components will be adjusted to achieve optimum yield commensurate with evenness and desired coating thickness. Suitable temperatures range from

40°C to 70°C preferably 50°C.

In the preparation of a particulate polymer for an electrorheological fluid, the pH will also be critical factor in that the extent of base "doping" of the polyaniline redox initiator affects the conductivity of the coated solid and, ultimately, the yield strength of the electrorheological fluid. Preferably the pH of the polyaniline is adjusted to pH 8 to 12, suitably about pH 10. Conversion to the base form of polymer may in some cases be carried out before the coating monomer is grafted on to the substrate particles e.g. for aniline polymers but in others it should be carried out after the coating step e.g. for poly-toluidines.

The invention will now be further described by way of example.

Example 1

Coating of Poly(o-toluidine) with Poly(lauryl methacrylate).

a) Preparation of Poly(o-toluidine hydrochloride)

0.8 moles of ortho toluidine was dissolved in 500ml of 2M hydrochloric acid and then chemically oxidised by a solution of 1 mole of ammonium persulphate in 1000ml of 2M hydrochloric acid. The reaction was well agitated and cooled in an ice bath to keep the temperature below 5°C. The resultant particles of poly(o-toluidine hydrochloride) were collected by filtration and washed with an excess of 2M hydrochloric acid. The material was then transferred to an extraction thimble and extracted with water overnight after which it was dried for 48 hours under vacuum at 50°C.

b) Coating of poly(o-toluidine hydrochloride) and its conversion to a base form.

Lauryl methacrylate was extracted with 1M sodium hydroxide solution, washed with water and then dried over anhydrous sodium sulphate. The poly(o-toluidine hydrochloride) was suspended in excess of this monomer (1g to 20cm^3) in a pyrex tube and after degassing the tube was sealed under vacuum. The reaction

mixture in the tube was heated to 50°C and reaction allowed to continue until the required level of polymer had formed, typically around 100% weight gain in 24 hours. The solid was then collected by filtering and washed with methanol, dried under vacuum for 12 hours at 50°C.

Figure 2 illustrates the effect of varying polymerisation time on the % weight gain of the substrate polymer particles.

For the purposes of ER fluid production, this material required conversion to a more basic form. Typically this was achieved by immersing the powder in excess pH 5 phosphate buffer (250ml per g) and leaving for 12 hours after which the base form was filtered off, extracted with water overnight and finally vacuum dried for 48 hours at 50°C.

c) ER Fluid Performance of coated poly(o-toluidine)

Table 1. shows a comparison of the performance in terms of static yield stress and current density of pH 5 poly(lauryl methacrylate) coated and uncoated poly(o-toluidine) dispersed in 20cS silicone oil at 0.2 volume fraction of solid.

Table 1

Field Strength (V/mm)	Static Yield Stress (kPa)		Current Density* ($\mu A/cm^2$)	
	Coated	Uncoated	Coated	Uncoated
800	0.15	0.5	0.50	1.25
1600	0.52	1.01	1.75	4.50
2400	0.89	1.51	4.00	12.00
3200	1.47	1.89	6.50	31.25
4000	1.84	2.76	10.50	56.25
4800	2.21	3.01	13.50	106.25

* Measured over a 0.5mm electrode gap.

Error in yield stress measurements +/-0.4kPa.

Example 2 Coating of poly(aniline) with poly(styrene)

a) Preparation of poly(aniline)

0.8 moles of aniline was dissolved in 500ml of 2M hydrochloric acid and then chemically oxidised by a solution of

1 mole of ammonium persulphate in 1000ml of 2M hydrochloric acid. The reaction was well agitated and cooled in an ice bath to keep the temperature below 5°C. The resultant particles of poly(aniline hydrochloride) were collected by filtration and washed with an excess of 2M hydrochloric acid.

In contrast to poly(o-toluidine), poly(aniline) can be successfully coated in the base form. This conversion was achieved by dispersing the hydrochloride in distilled water and the pH of the dispersion was adjusted to pH10 using 1M sodium hydroxide. The solution volume was doubled with a borate based pH10 buffer solution and the system left to equilibrate overnight. The solid was then collected by filtration and washed with water before being extracted for 12 hours with water and dried under vacuum for 48 hours at 50°C.

b) Coating of poly(aniline)

As supplied Styrene was distilled at reduced pressure. The poly(aniline) was suspended in excess of this monomer (1g to $20cm^3$). The reaction mixture was heated to 50°C and reaction allowed to continue until the required level of polymer had formed, typically around 100% weight gain in 24 hours. The solid was then collected by filtering and washed with methanol, dried under vacuum for 12 hours at 50°C.

c) ER Fluid Performance of Coated Poly(aniline)

Table 2. Below shows a comparison of the performance of pH 10 poly(styrene) coated and uncoated poly(aniline) dispersed in 20cS silicone oil at 0.2 volume fraction of solids.

Table 2.

Field Strength (V/mm)	Static Yield Stress (kPa)		Current Density* ($\mu A/cm^2$)	
	Coated	Uncoated	Coated	Uncoated
800	0.24	0.31	0.50	1.25
1600	0.55	0.92	1.25	2.50
2400	0.74	1.01	3.75	5.00
3200	0.77	1.26	2.50	7.50
4000	1.44	1.78	6.25	10.00

* Measured over a 0.5mm electrode gap.

Error in yield stress measurements +/-0.4kPa.

Example 3

Coating of poly(aniline) with poly(styrene) by emulsion polymerisation

As supplied Styrene was distilled at reduced pressure. 50ml of this monomer was added to 100ml of water. To this mixture 10ml of Triton X 100 was added. On stirring this formed an emulsion in whch 25g of 25g of the poly(aniline) was suspended. The reaction mixture was refluxed for 3-4 hours. The solid was then collected by filtering, washed with methanol and dried under vacuum for 48 hours at 50°C.

Example 4

Coating of poly(aniline) with poly(styrene) by solution polymerisation

As supplied Styrene was distilled at reduced pressure. 50ml of this monomer was added to 100ml of solvent, typically n-hexane. To this solution 25g of poly(aniline) was added. The reaction mixture was refluxed for 2 hours. The solid was then collected by filtering, washed with petroleum spirit (bp 60-80) and dried under vacuum for 12 hours at 50°C.

CLAIMS

1. A process of modifying the surface of an electrorheologically functional polymer characterised in that the polymer is one capable of acting as a redox initiator of polymerisation and is modified by polymerisation of an olefinically unsaturated monomer at the polymer surface.

2. A graft copolymer of an electrorheologically functional polymer and a vinyl monomer.

3. A process for the preparation of a coated solid substrate comprising effecting polymerisation of at least one coating monomer in the presence of a surface of an electrorheologically functional polymer capable of acting as the redox initiator for the polymerisation of the monomer.

4. A process according to claim 3, in which the polymer substrate is polyaniline or a poly substituted aniline.

5. A process according to claim 3 or 4, in which the coating monomer is selected from alkenes and unsaturated esters.

6. A process according to claim 5, wherein the coating monomer is an alkyl methacrylate containing up to 20 carbon atoms in the alkyl group.

7. A process according to any of claims 3 to 6, in which the polymer substrate is present in particulate form and the coated solid is in the form of coated particles.

8. A process according to any of claims 3 to 7, wherein the polymer substrate is a coating on a further material.

9. A process according to any of the preceding claims wherein the polymerisation is effected by bulk polymerisation.

10. A coated solid when prepared by the process of any of claims 3 to 9.

11. An electrorheological fluid which comprises a liquid continuous phase and a coated solid in accordance with claim 10 dispersed therein.

12. An electrorheological fluid according to claim 11, wherein the coated solid is lauryl methacrylate-coated poly(o-toluidine).

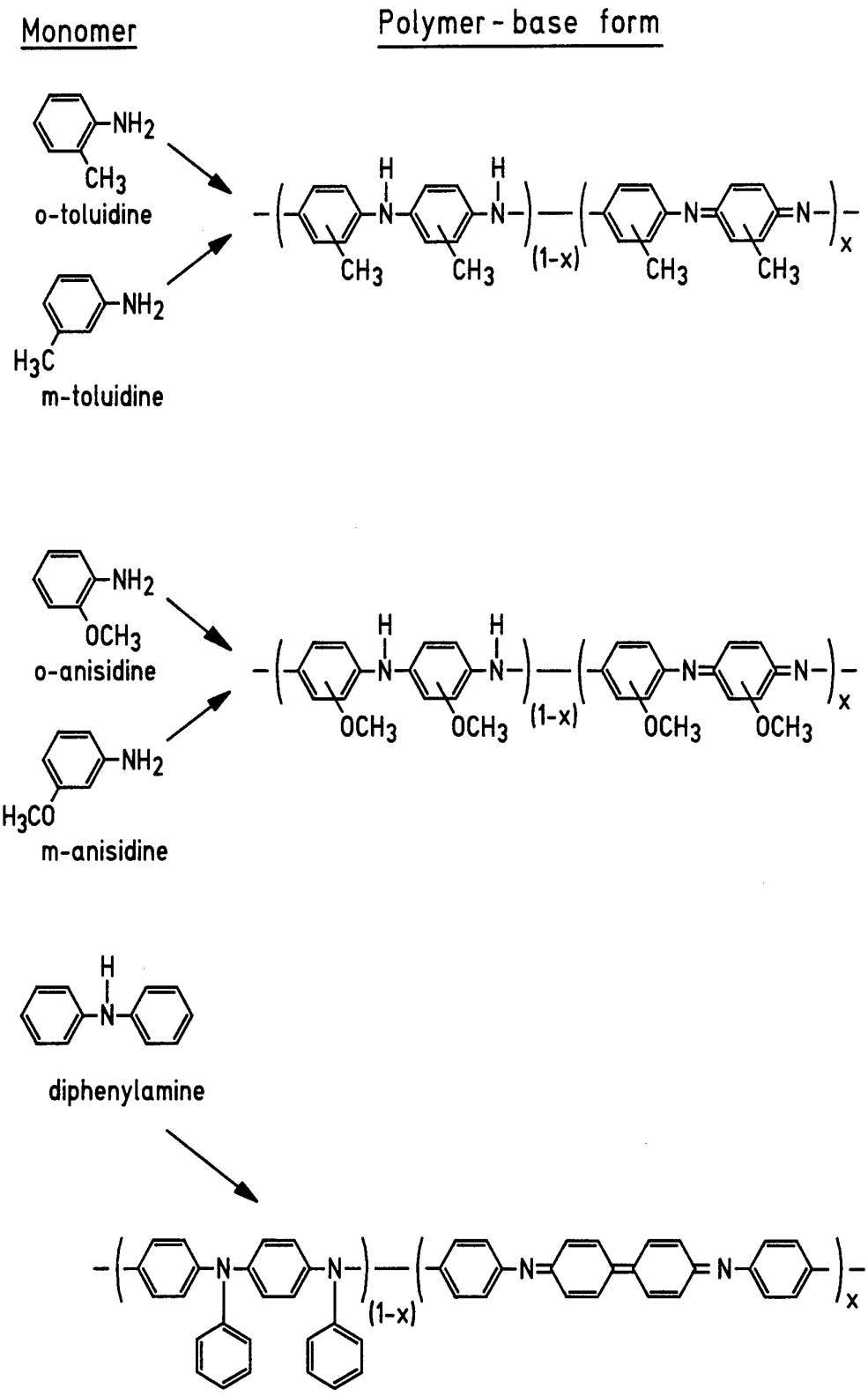
Monomer
Polymer - base form
o-toluidine
m-toluidine
o-anisidine
m-anisidine
diphenylamine
(1-x)
x

Fig. 1

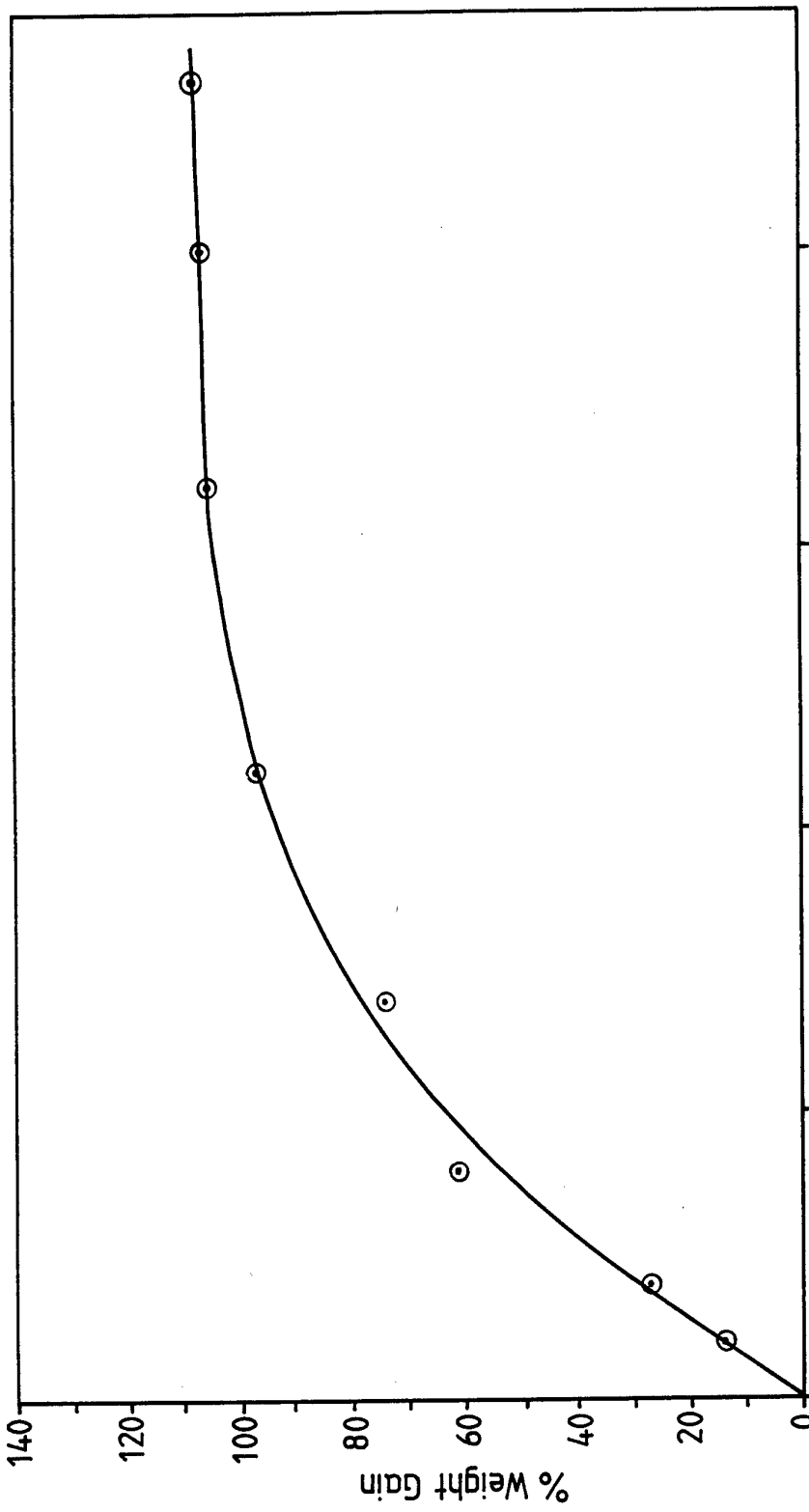

Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/01275

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D4/06 C10M171/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C10M C08F C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MOLECULAR CRYSTALS AND LIQUID CRYSTALS, vol.121, 1985 pages 173 - 180 MACDIARMID ET AL. 'Polyaniline : interconversion of metallic and insulating forms' cited in the application	1
A	EP,A,0 512 926 (ALCATEL) 11 November 1992	2-12
A	EP,A,0 455 224 (TOMOEGAWA PAPER) 6 November 1991	2-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 September 1994	13. 10. 94

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 94/01275

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		JP-T-	6501976	03-03-94
EP-A-0455224	06-11-91	JP-A-	4293924	19-10-92
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