

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 482 663 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91118246.7**

(51) Int. Cl.⁵: **C10M 171/00**

(22) Date of filing: **25.10.91**

(30) Priority: **25.10.90 JP 288113/90**

(43) Date of publication of application:
29.04.92 Bulletin 92/18

(84) Designated Contracting States:
BE DE FR GB

(71) Applicant: **Dow Corning Toray Silicone
Company, Limited**
Mitsui Bldg. No. 6, 2-3-16,
Nihonbashi-Muromachi, Chuo-Ku
Tokyo 103(JP)

(72) Inventor: **Nakamura, Takashi**
6, 1-chome, Yushudai Nishi
Ichihara-shi, Chiba Prefecture(JP)

(74) Representative: **Spott, Gottfried, Dr.**
Spott Weinmiller & Partner
Sendlinger-Tor-Platz 11
W-8000 München 2(DE)

(54) **Electroviscous fluid.**

(57) The electroviscous fluid according to the present invention comprises a dispersion of wet-method silica particles having an average particle diameter of 10 to 500 micrometers and having a pH of not greater than 6.5 in an electrically insulating fluid. The fluids of this invention are characterized by a substantial increase in yield value at low voltages and excellent shear stability.

EP 0 482 663 A1

The present invention relates to an electroviscous fluid which comprises a dispersion of wet-method silica particles in an electrically insulating fluid.

Fluids whose viscosity can be varied by the application of an external voltage have received attention in the last several years because they may be used for applications such as drive power transmission, impact absorption, valve-like behavior, and so forth.

Such fluids whose viscosity is increased by means of an electric field are generally called "electroviscous fluids". However, in order to be able to withstand the severe service in, for example, a clutch, engine mount, or shock absorber, a fluid is required which undergoes a substantial increase in yield value at low voltages.

Various types of these fluids have already been proposed, and they are typified by, for example, dispersions of porous inorganic particles (e. g., silica, alumina, talc) in an electrically insulating fluid. In each case, through the formation of an electrical double layer by means of water adsorbed on the particle surfaces, the particles become oriented in response to an external electric field and the viscosity increases (more specifically, the fluid is converted into a Bingham fluid, which exhibits a yield value). This effect is called the "Winslow effect". The following disadvantages have been associated with silica-based electroviscous fluids: they have limited application temperatures (approximately 10 ° C to 80 ° C), they abrade the surrounding machinery, and the particles form a sediment. Still, since silica is easily obtained on an industrial basis and is highly susceptible to improvement and manipulation, it has been considered potentially useful for certain sectors of application, for example, machinery which would be used in a room temperature environment and which would undergo little abrading motion. Silica-based electroviscous fluids are disclosed in United States Patent Number 3,047,507 and in Japanese Patent Application Laid Open [Kokai or Unexamined] Number 61-44998 [44,998/86], but in each case these exhibit an impractically weak Winslow effect.

The present inventor carried out extensive investigations with a view to solving the aforementioned problems, and discovered as a result that the aforementioned problems are substantially reduced by the use of a particular type of wet-method silica in such electroviscous fluids. The present invention was developed based on this discovery.

It is an object of the present invention to introduce an electroviscous fluid which exhibits excellent properties, for example, which undergoes a substantial increase in yield value at low voltages.

The object of this invention is also to provide an electroviscous fluid which comprises a dispersion of wet-method silica particles in an electrically insulating fluid, but which is further characterized by wet-method silica particles having an average particle diameter of 10 to 500 micrometers and having a pH not exceeding 6.5 when tested as a 4 percent aqueous suspension.

Figure 1 reports the relationship between the shear rate and shear stress for the electroviscous fluid prepared in Example 1, and Figure 2 reports the relationship between the shear rate and shear stress for the electroviscous fluid prepared in Comparison Example 2.

The present invention utilizes wet-method silica particles which comprise the essential component for imparting a strong Winslow effect. These wet-method silica particles are prepared by the production of silica by the addition of acid under wet conditions to water glass starting material. These wet-method silica particles are an ideal disperse phase for electroviscous fluids because their surfaces possess a layer of adsorbed water, which is ideal for the development of the Winslow effect, and because they have optimal particle sizes. The average particle size should fall within the range of 10 to 500 micrometers and preferably falls within the range of 50 to 200 micrometers. When the particle size is less than 10 micrometers, the particles exhibit a large orientability, but the interparticle forces are small and a satisfactory viscosity will not be achieved. On the other hand, at particle sizes in excess of 500 micrometers, the orientability is diminished and the thickening effect is reduced. Moreover, at such dimensions, the particle size itself begins to pose significant problems. The particle shape should be as close to truly spherical as possible. When the particles substantially deviate from spherical, the effective interparticle contact area declines and the cohesive forces are then weak. With regard to the particle size distribution, the narrower the better. The particle orientability becomes increasingly uniform as the particle size distribution becomes narrower, which provides for a more efficient viscosity rise. Various methods can be devised for the production of silica particles which have a narrow particle size distribution and are as close to spherical as possible, but such particles are obtained mainly by devising a suitable drying process. For example, spray drying methods are ideal.

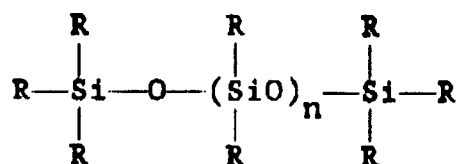
In addition to the properties discussed above, the quantity of ion in wet-method silica particles is also a crucial factor in determining the magnitude of the Winslow effect. While not limiting the present invention with any particular theory, the inventor believes that the principal ion present in the silica is the sodium ion, and this is mainly the excess from the sodium ion used for neutralization of the solid acid present as an

impurity in the water glass starting material. Accordingly, the fluidity of the silica is governed by the magnitude of this quantity of sodium ion. According to experiments by the inventor, the presence of free ion in the silica brings about a retardation in particle orientation. A clear example of this phenomenon is the instability in shear stress at a constant or variable shear rate that is observed when an electric field is applied to an electroviscous fluid prepared by the dispersion of free ion- containing wet-method silica. In the case of free ion- containing particles, this is thought to be due to an increase in the time required for orientation of the randomly distributed particles due to the relatively long time associated with ion movement. The result is the appearance of instability under dynamic conditions. It is for this reason that wet-method silica particles depleted of free ion (e. g., sodium ion, etc.) are optimal for the development of a useful Winslow effect. Pure wet-method silica particles generally exhibit fluidity in the acid region, i. e., acidic silica is ideal. The fluidity index according to the present invention is characterized by the following: the pH of the 4 weight percent aqueous suspension of the silica particles must not exceed 6.5, and more preferably does not exceed 5.5. A useful Winslow effect does not appear at pH values in excess of 6.5. In order to obtain wet-method silica particles which have such a fluidity index, the excess sodium ion must be removed to the maximum possible extent, or, alternatively, a pure water glass which contains only traces of solid acid must be employed as the starting material. The pH of the wet-method silica particles are tested in a 4 weight percent aqueous suspension prior to addition of the particles to the electrically insulating fluid.

No specific restrictions are placed on the wet-method silica particles employed by the present invention as long as they satisfy the conditions discussed above. They may be selected from among commercial wet-method silica particles, for example, Nipsil AQ-S from Nippon Silica Kogyo Kabushiki Kaisha and its equivalents.

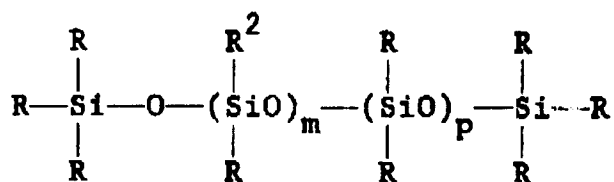
The electroviscous fluid according to the present invention comprises the dispersion of wet-method silica particles as described hereinbefore in an electrically insulating fluid. However, the electrically insulating fluid itself is not particularly restricted as long as it is a liquid at room temperature and is electrically insulating. Such electrically insulating fluids are exemplified by mineral oils, dibutyl sebacate, chlorinated paraffins, fluorine oils, and silicone oils.

Among the preceding, silicone oils are preferred for their strong electrical insulation, low temperature-dependent viscosity variation, and so forth. The silicone oils are exemplified by the fluid diorganopolysiloxanes with the following chemical structure:



wherein each R denotes a monovalent hydrocarbon group as exemplified by alkyl groups such as methyl, ethyl, and propyl, and aryl groups such as phenyl. It is preferred that at least 30% of the R groups are methyl groups. Moreover, while the degree of polymerization of n is not particularly specified, it is preferable that n does not exceed 1,000 in order to achieve a practical viscosity range. Values not exceeding 100 are even more preferred. Silicone oils with this structure are available in the form of a large number of commercial products, for example, SH200 from Toray Dow Corning Silicone Company, Limited.

Furthermore, among the silicone oils, fluoroalkyl- containing diorganopolysiloxanes are particularly preferred because they enhance the Winslow effect and inhibit the particle sedimentation caused by specific gravity differences. These are concretely expressed by the following structural formula:



wherein R is defined as above, R² is a fluoroalkyl group having 10 or fewer carbons, and m and p are integers with values not exceeding 1,000.

The structure of the aforementioned C<10 fluoroalkyl group is not particularly specified, but the 3,3,3-trifluoropropyl group is preferred from the standpoint of ease of synthesis. In order to obtain a substantial enhancement of the Winslow effect, it will be preferable for each molecule to contain at least 30 mole percent fluoroalkyl group. Furthermore, methyl should comprise at least 30% of the R groups from the standpoints of material acquisition and economics. While the degree of polymerization m is again not particularly specified, it preferably does not exceed 1,000 in order to achieve a practical viscosity range. Values not exceeding 100 are even more preferred. The mechanism by which the fluoroalkyl group enhances the Winslow effect is not clear. While not limiting the present invention with any particular theory, the inventor believes that a strong intramolecular dipole is generated by the simultaneous presence in the molecule of the electronegative fluorine atom and electropositive silicon atom separated by a suitable distance. Polarization of the double layer is then promoted by contact between this dipole and the electrical double layer on the wet-method silica particle. Otherwise, fluorine-containing fluids tend to have larger specific gravities, which results in a concomitant inhibition of silica particle sedimentation. These fluoroalkyl-containing diorganopolysiloxanes are commercially available, for example, as FS1265 from Toray Dow Corning Silicone Company, Limited.

The electroviscous fluid according to the present invention comprises the dispersion of wet-method silica particles as described hereinbefore in an electrically insulating fluid as described hereinbefore. The quantity dispersed should fall within the range of 0.1 to 50 weight percent and preferably is in the range of 10 to 40 weight percent. A satisfactory thickening effect is not obtained at less than 0.1 weight percent. At values exceeding 50 weight percent, the viscosity of the electroviscous fluid is so substantially increased as to be impractical.

The electroviscous fluid according to the present invention as described above is useful as the working oil or functional oil in particular types of machinery, for example, machinery which will be employed in the vicinity of room temperature and where there will be little abrading motion.

The present invention will be explained in greater detail below through the use of illustrative and comparison examples. In the examples, parts = weight parts, cs = centistokes, and the viscosity is the value at 25 °C.

The electroviscous behavior was measured as follows. The test fluid was placed in an aluminum cup (interior diameter = 42 millimeters (mm)) into which an aluminum rotor (diameter = 40 mm, length = 60 mm) was subsequently inserted. The resulting cylindrical cell was set up vertically, and the cup was linearly accelerated from a shear rate (D) of zero to 330 s⁻¹ over 40 seconds. During this period, the torque applied to the rotor was measured with a torque sensor, and this was converted into the shear stress (S) and the D-versus-S curve was drawn on an X-Y recorder. In addition, the rotor was electrically grounded and D-versus-S curves were also recorded while applying a direct-current voltage to the cup. The intersection of the extrapolation of the linear segment with the S-axis was designated as the yield value at the particular field strength. The stability of the shear stress and the sedimentability of the wet-method silica particles were also examined.

In the following examples all amounts (parts and percentages) are by weight unless otherwise indicated.

Example 1

15 Parts wet-method silica particles (Nipsil AQ-S from Nippon Silica Kogyo Kabushiki Kaisha) with an average particle size of 100 micrometers and a pH of 5.5 to 6.5 (pH was tested in a 4 weight percent aqueous suspension) was added with stirring to 85 parts aliphatic hydrocarbon oil with a viscosity of 100 cs (Rubber Swelling Oil No. 3 from Nippon Sekiyu Kabushiki Kaisha) to afford an electroviscous fluid in the form of a suspension in which the wet-method silica particles were dispersed in the aliphatic hydrocarbon oil.

The electroviscous behavior of this fluid was then measured, and the measurement results are reported in Table I and Figure 1 below. The three lines in Figure 1 represent the yield values tested at 0, 1, and 2 KV/mm.

Example 2

15 Parts wet-method silica particles (Nipsil AQ-S from Nippon silica Kogyo Kabushiki Kaisha) with an average particle size of 100 micrometers and pH of 5.5 to 6.5 (pH was again tested in a 4 weight percent aqueous suspension) was added with stirring to 85 parts trimethylsiloxy-terminated polydimethylsiloxane (viscosity = 100 cs) to give an electroviscous fluid in which the wet-method silica was uniformly dispersed in the polydimethylsiloxane.

The electroviscous behavior of this fluid was then measured, and the measurement results are reported in Table I below.

Example 3

An electroviscous fluid was prepared as in Example 2, but in this case using a trimethylsiloxy-terminated poly(methyl-3,3,3-trifluoropropyl)siloxane (viscosity = 300 cs) in place of the polydimethylsiloxane (viscosity = 100 cs) used in Example 2. The properties of this fluid were measured as in Example 2, and these measurement results are reported in Table I below.

Comparison Example 1

An electroviscous fluid was prepared as in Example 2, but in this case using wet-method silica particles (Nipsil L- 300 from Nippon Silica Kogyo Kabushiki Kaisha) with an average particle size of 4 micrometers and pH = 5.5 To 6.5 (pH again was tested in a 4 weight percent aqueous suspension) in place of the wet-method silica particles with average particle size = 100 micrometers used in Example 2. The properties of this fluid were measured as in Example 2.

These measurement results are also reported in Table I.

Comparison Example 2

An electroviscous fluid was produced as in Example 2, but in this case using wet-method silica particles (Nipsil NA-R from Nippon Silica Kogyo Kabushiki Kaisha) with an average particle size of 85 micrometers and pH = 10.0 to 11.0 (tested in a 4 weight percent aqueous suspension) in place of the wet-method silica with average particle size = 100 micrometers used in Example 2. The electroviscous behavior of this fluid was then measured, and the results reported below in Table I and Figure 2 were obtained. Again, the three lines in Figure 2 represent the yield values tested at 0, 1, and 2 KV/mm.

Table I

	yield value (Pa)		shear stress stability	particle sedimentability
	1 KV/mm	2 KV/mm		
Example 1	170	280	high	moderate
Example 2	220	460	high	moderate
Example 3	280	590	high	low
Comparison Example 1	110	200	high	moderate
Comparison Example 2	160	230	low	moderate

The Examples delineated hereinabove show the electroviscous fluid according to the present invention which employs wet-method silica particles with an average particle size of 10 to 500 micrometers and a pH (hydrogen ion concentration) not exceeding 6.5, wherein the pH of the wet- method silica particles was tested in a 4 weight percent aqueous suspension prior to addition of the particles to the electrically insulating fluid. The fluids of the invention display excellent electroviscous behavior, i.e., a substantial increase in yield value at low voltages and an excellent shear stability.

Claims

1. In an electroviscous fluid comprising a dispersion of silica particles in an electrically insulating fluid, the improvement comprising using wet-method silica particles having an average particle diameter of 10 to 500 micrometers and having a pH of not greater than 6.5.

Figure 1

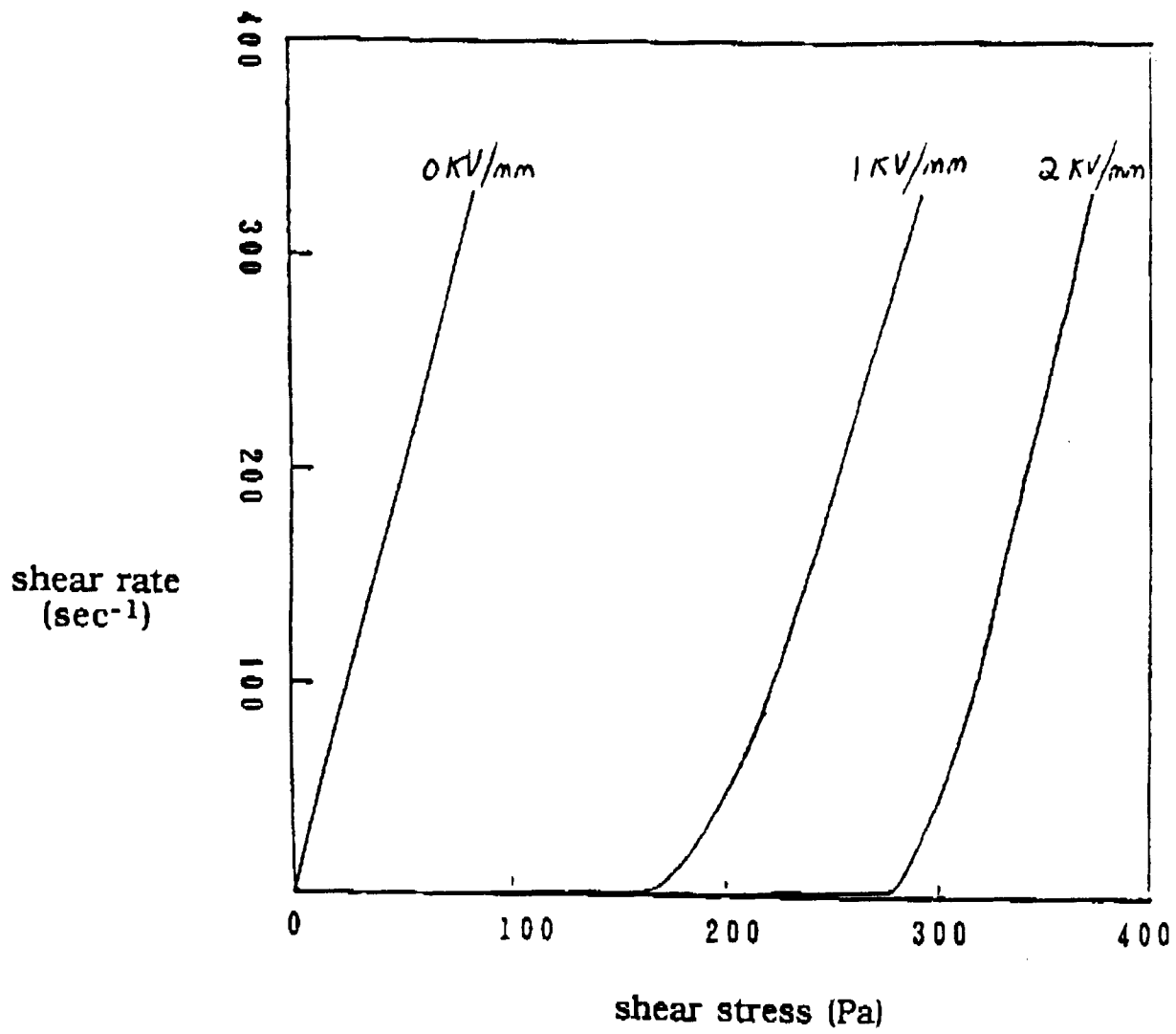
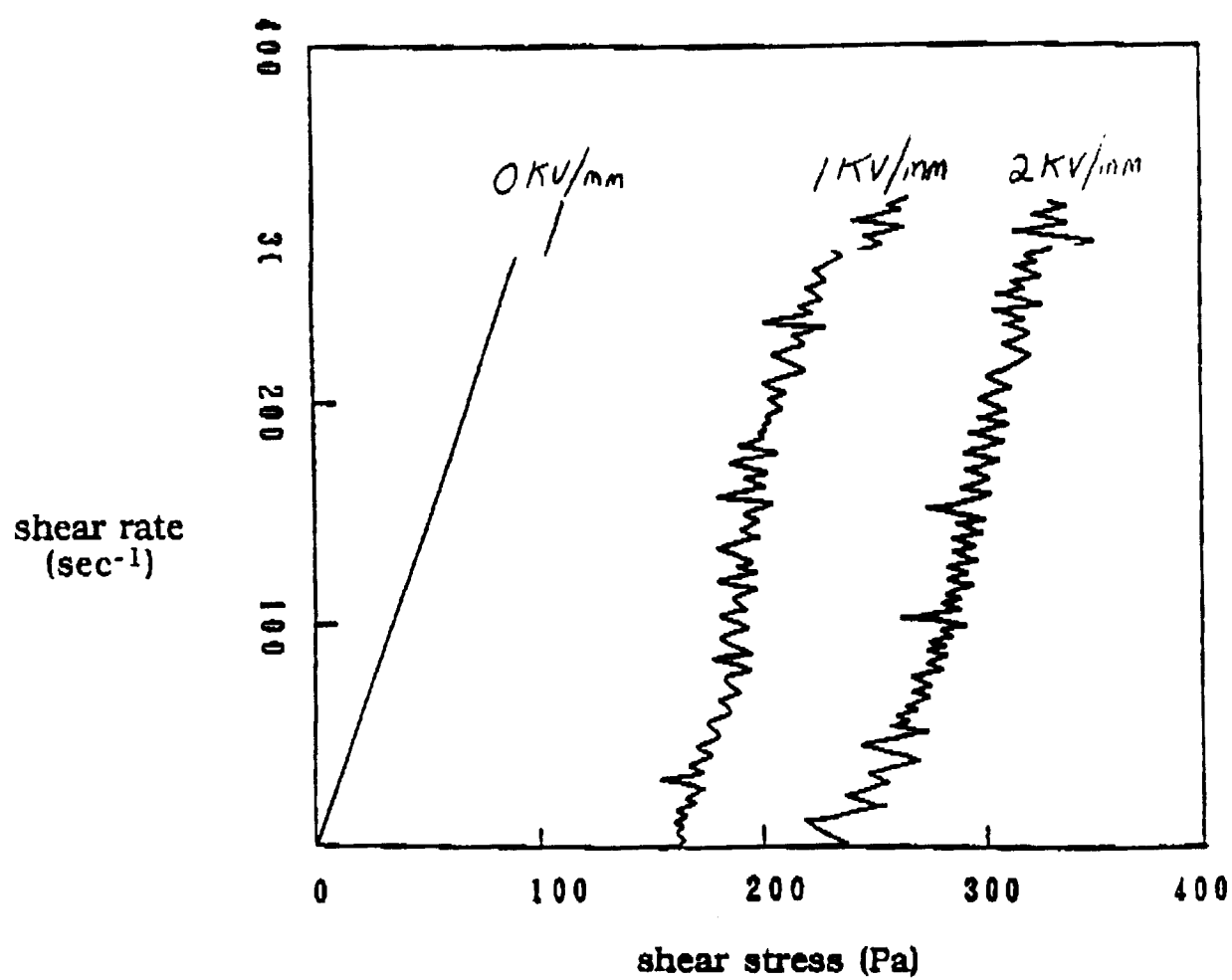


Figure 2





European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 8246

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	EP-A-0 342 041 (TOA NENRYO KOGYO K.K.) * claims 1-6,10; examples 1-8 ** — — —	1	C 10 M 171/00
Y	EP-A-0 311 984 (AMERICAN CYANAMID COMP.) * page 3, line 44 - line 52; claims 1-21 ** — — — — —	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 23 December 91	Examiner DE LA MORINERIE B.M.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			