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(54) Electrorheological fluids.

(57) An electrorheological fluid comprises a low dielectric constant fluid having dispersed therein a discrete phase comprising at least one of

(a) a particulate solid bearing a coating of a high conductive constant aprotic material, or

(b) a particulate layered mixed metal hydroxide, or

(c) a particulate layered mixed metal hydroxide bearing a coating of said aprotic material.

The electrorheological fluids have improved thermal stability and provide a strong and rapid response to low electric field strengths as compared to previously known electrorheological fluids which rely on the presence of water for the response to an electric field.

EP 0 427 520 A1

ELECTRORHEOLOGICAL FLUIDS

This invention relates to electrorheological fluids (ERFs), i.e. fluids which exhibit a significant change in flow properties when exposed to an electric field. These fluids are also known as "electric field responsive fluids," "electro-viscous fluids" or "jammy fluids."

Early studies of electrorheological fluids (ERFs) demonstrated that certain suspensions of solids (a 1,di screte," "dispersed" or "di scont i nuous" phase) in liquids (a "continuous" phase) show large, reversible electrorheological effects. These effects are generally as follows: in the absence of an electric field, electrorheological fluids (ERFs)-exhibit Newtonian flow properties. Specifically, the shear stress (applied force per unit area) is directly proportional to the shear rate applied (relative velocity per unit thickness). When an electric field is applied, a yield stress phenomenon appears and no shearing takes place until the shear stress exceeds a minimum yield value which increases with increasing field strength, i.e. the fluid appears to behave like a Bingham plastic. This phenomenon appears as an increase in apparent viscosity of several, and indeed many, orders of magnitude.

ERFs change their characteristics very rapidly when electric fields are applied or released, typical response times being on the order of 1 millisecond. The ability of ERFs to respond rapidly to electric signals make them uniquely suited for use as elements in electromechanical devices. Often, the frequency range of a mechanical device can be greatly expanded by using an ERF element rather than an electromechanical element having a response time which is limited by the inertia of moving mechanical parts. Therefore, ERFs offer important advantages in a variety of mechanical systems, particularly in those which require a rapid response between electronic controls and mechanical devices.

A range of devices have been proposed to take advantage of the electrorheological effect. Because of the potential for providing a rapid response interface between electronic controls and mechanical devices, it has been suggested that these fluids be applied in a variety of mechanical systems such as electromechanical clutches, fluid-filled engine mounts, high-speed valves with no moving parts, and active dampers for vibration control, among others.

As used herein, the term "dielectric" refers to substances having very low electrical conductivity, if any. Such substances generally have conductivities of less than 1×10^{-6} mho per centimeter. While a number of theories have been proposed to explain the electrorheological effect, a comprehensive theory explaining all of the observed phenomenon has not yet been developed.

There yet exists a need for an ERF that will operate at the relatively high temperatures encountered in commercial applications, while requiring a low electric field strength to produce a strong rheological response and wherein the discrete phase is present in low concentration. In ERFs which depend on the presence of free water or adsorbed water, the use of high stemperature is detrimental in that it tends to drive out the water and reduce the effectiveness of the fluid.

We have now prepared novel electrorheological fluids (ERFs) which do not require the presence of water in order to be effective.

These novel ERFs comprise a continuous liquid phase characterized as a dielectric fluid having a relatively low dielectric constant and a disperse phase characterized as either:

(a) a particulate solid of fine non-conductive particles bearing an aprotic coating, said coating having a relatively high dielectric constant, applied to the surface of the particles, or

(b) as being crystalline layered mixed metal hydroxide (herein referred to as "LMMH"), or

(c) as being crystalline LMMH having an aprotic coating applied to the surface of the particles.

As used herein, the expression "relatively low dielectric constant" of the dielectric continuous phase is used to contrast it with the higher "relatively high dielectric constant" of the dielectric disperse phase.

In some embodiments of the present invention, ERFs utilize particles of crystalline Las (Las) as the discrete phase. These Las may be represented by the formulae:

I $Mg_xAl_y(OH)_z$, and

II $Li_mD_dT(OH)_{(m+2d+3+na)}(A^n)_a$

where in Formula I:

x represents an average value of 1.7, y represents an average value of 0.5, and z represents an average value of 5; and

where in formula II:

m represents the number of Li cations present; D represents divalent metal cations; and d is the number of cations D in the formula; T represents trivalent metal cations; A represents monovalent or polyvalent anions other than OH^- ions; a is the number of anions A in the formula; n is the valence of A; and where $(m+2d+3+na)$ is equal to or greater than 3. It will be understood that since "n" represents a negative value and "a" represents a positive value, then n times a (na) will be negative. These LMMHs are preferably prepared by an instantaneous ("flash") coprecipitation wherein solu-

ble compounds, e.g. salts, of the metals are intimately mixed (using non-shearing agitation or mixing) with an alkaline material which supplies hydroxyl groups to form the mixed metal hydrous oxide crystals. A distinguishing feature of the present composition is that the crystals are essentially monolayer, or one layer of the mixed metal hydroxide per unit cell, which we call "monodispersed" crystals when they are in a liquid carrier, meaning that they are individual crystals of crystalline monolayer mixed metal hydroxides usually having crystal thicknesses in the range of 0.8 to 1.6 nm (8 to 16 A^0).

In the above formula, m is zero to 1, most preferably 0.5 to 0.75, when not zero.

The D metal is Mg, Ca, Ba, Sr, Mn, Fe, Co, Ni, Cu, or Zn, most preferably, Mg, Ca, or mixtures of these, and the value of d is zero to 4, preferably 1 to 3 and most preferably 1, though m+d is not zero.

The T metal is Al, Ga, Or, or Fe, preferably Al and Fe, and most preferably Al.

The A anions are monovalent or polyvalent, and they can include inorganic ions such as halide, sulfate, nitrate, phosphate, carbonate, most preferably halide, sulfate, phosphate, or carbonate, or they may be hydrophilic organic ions such as glycolate, lignosulfonate, polycarboxylate, or polyacrylates. These anionsoften are the same as the anions which form part of the metal compound precursors from which these novel crystals are formed.

An example of an alkoxide-based LMMH, such as one shown in formula 1, useful in the present invention may be prepared by the following general chemical reaction:

A) $(M_1^{+x})(OC_yH_{2y+1})_x + (M_2^{+z})(OC_nH_{2n+1})_z + H_2O = M_1^{+x}M_2^{+z}(OH)_{x+z} + C_yH_{2y}OH + C_nH_{2n}OH$

wherein:

M_1 is a divalent metal cation, such as Mg;

M_2 is a trivalent metal cation, such as Al;

y is from 1 to 4;

n is from 1 to 4;

and the amount of H_2O is sufficient to provide sthe requisite amount of OH' anions to satisfy the requirements of the metal cations in the formula.

The reaction is relatively slow and the total yield is limited by the extent of solubility of the metal alkoxides in alcohol or other solvents in which the reaction is carried out. As a general rule, a metal alkoxide is most soluble in its corresponding alcohol. However, solubility is only of the order of 1 percent by weight in most cases with the notable exception of magnesium ethoxide in ethanol.

At the outset, the preparation of the formula 1 alkoxide-based LMMHs should be conducted in an environment which is essentially free of water. Since the beginning metal alkoxides are hygroscopic, and can react to form hydroxide, carbonate and alcohol before the LMMH has formed, it is sometimes necessary to control local environment. Consequently, the use of nitrogen-purged, moisture-free apparatus is recommended during the initial mixing of the beginning metal alkoxides.

In general, two metal alkoxides in powder form are blended together and then added to dry alcohol in the approximate weight ratio of alkoxide:alcohol of 1:50. This mixture is stirred while heating to 50 ° C to obtain a solution which may still contain some undissolved solids. These solids may be separated by vacuum filtration. The filtrate is then treated with two drops (0.06g) of deionized water for each 1 g of alkoxide while stirring. The filtrate obtained may be allowed to stand for 1 hour to 48 hours. Forty to fifty percent of the solvent is then evaporated, for instance, by flowing nitrogen to produce an LMMH-containing gel. In some instances a gel may form prior to the sevaporation step, in which case this step may be eliminated.

In order to produce the more specific embodiment, $Mg_xAl_y(OH)_z$, the above procedure may be followed. It is preferred that the magnesium and aluminum ethoxides be combined in methanol.

Methods for preparing the LMMHs of formula II above that are useful in the invention ERFs are disclosed in EP-A-0.207.811 to Burba, et al. The Burba patent indicates that in order to produce a LMMH, a mixture of the selected soluble metal compounds, especially the acid salts (e.g. chloride, nitrate, sulphate, phosphate, etc.) are dissolved in an aqueous carrier. The ratios of the metal ions in the solution are predetermined to give the ratios desired in the final product. The concentration limit of the metal compounds in the solution is governed, in part, by the saturation concentration of the least soluble of the metal compounds in the solution. Any non-dissolved portions of the metal compounds may remain in the final product as a separate phase, which is not a serious problem, usually, if the concentration of such separate phase is a relatively low amount in comparison to the soluble portions, preferably not more than 20 percent of the amount of soluble portions. The solution is then mixed rapidly and intimately with an alkaline source of OH- ions while substantially avoiding shearing agitation thereby forming monodispersed crystals of LMMH. One convenient way of achieving such mixing is by flowing the diverse feed streams into a mixing tee from which the mixture flows, carrying the reaction product, including the monodispersed LMMHs of the above formula 1. The mixture may then be filtered, washed with fresh water to remove extraneous soluble ions (such as Na^+ or NH^+ ions, and other soluble ions) which are not part of the desired product, and dried

to remove unbound water.

One method of preparing the formula II LMMH composition, however not exclusively the only method, is to react a solution' of metal salts such as magnesium and aluminum salts (approximately 0.25 molar) with an appropriate base such as ammonia or sodium hydroxide in quantities sufficient to precipitate the LMMH. For ammonium hydroxide, the most preferable range is 1 to 1.5 equivalents of OH- per equivalent of salt anion. The precipitation should be done with little or no shear so that the resultant flocs are not destroyed. One method of accomplishing this is to flow two streams, the salt stream and the base stream, against one another so that they impinge in a low shear, converging zone such as would be found in a mixing tee. The reaction product is then filtered and washed, producing a filtercake of 10 percent solids and dried to remove unbound water.

LMMHs may be prepared to obtain a relatively narrow distribution of particle sizes. It is believed that this has significant consequences since the electrorheological effect is believed to be proportional to both surface charge and the surface to mass ratio or aspect ratio. Consequently, high aspect ratios are desirable and LMMHs have aspect ratios, generally ranging from 30 to 650, with aspect ratios of 600 being readily obtained.

The LMMH-based ERFs are characterized in that they have little or no unbound or free water, preferably no unbound or free water, are heat stable, require a low concentration of the discrete phase, are responsive to low applied field strengths and provide a strong electrorheological response so that they may be usefully employed in a variety of applications. It is believed that ERFs which contain LMMH particles exhibit strong electrorheological response because of the high surface area per unit of mass of the particles which enables the achievement of a high surface charge to mass ratio.

In EP-A-0.207.811 the LMMRs are shown, for elample, as being prepared by mixing together the requisite metal salts, such as $MgCl_2$ and $AlCl_3$, in the desired ratio and then reacting the mixture with a source on OH ions, such as NH_4OH, in order to produce monodispersed, monolayer crystals, each of which contains both the metals as hydrated metal oxides. There may be found in the crystals a very small amount of the chloride ion due to incomplete conversion. In more recent work with that type of reaction, mixtures of metal alkoxides have been reacted with a source of OH ions to form the monolayer, monodispersed crystals of mixed metal hydroxides in which there can be no residual chlorine, since the beginning metal compounds did not contain chlorine. Any of those LMMHs can be used in the present invention, but those made from the compounds free of halogens are preferred, especially due to the possibility that halide ions might tend to be corrosive in some applications, especially if some free (unbound) water is permitted to enter the fluid.

The continuous phase of the ERF employing LMMH as the discrete phase comprises a liquid, semi-solid or gel composition and may be selected from those dielectric fluids having a relatively low dielectric constant usually of 40 to 1, preferably less than 35 and most preferably less than 5. These compositions include polyglycols, alcohols, polyols, hydrocarbons, halogenated hydrocarbons, mineral oils, silicone-based oils and greases, ethers, ketones and the like in either liquid, gel or semi-solid form. However, the continuous phase is preferably selected from hydrocarbons or mineral oils and is most preferably silicone-based oils. Operating factors such as, for instance, operating temperature, should be taken into account in selecting the continuous phase composition to optimize the ERF composition for particular applications.

The LMMH crystals are positively charged and are consequently less readily dispersed in non-polar than in polar fluids such as alcohols. Thus, when the LMMH is to form the sole component of the discrete phase, the choice of continuous phase is restricted to those in which the is dispersible up to the required weight proportion. However, it is often desired to use as a continuous phase a fluid in which the LMMH is not readily dispersed. In this event, the LMMH may be modified to render it more readily dispersible. The modification may be effected by treating the LMMH crystals with a functionalizer, for example an aliphatic carboxylic or fatty acid, such as, for instance, stearic acid. Alternatively, steps may be taken to otherwise neutralize the LMMH crystal's surface charge. Such neutralization may be effected by combining the LMMH with a dispersible negatively-charged functionalizing species. For example, a synthetic clay such as LAPONITE, containing no free moisture, may be combined with an amine salt to form a composition that is readily dispersible in mineral oil. This clay-amine composition may then be combined with the LMMH crystals to form a complex that is readily dispersed in non-polar fluids thereby greatly expanding the range of fluids usable as the continuous phase of the invention ERFs. Furthermore, since these non-polar fluids are often the most desirable continuous phase fluids because of their low dielectric constants, the complexing or functionalizing of the LMMHs allows the production of ERFs having greater electrorheological response.

The discrete phase LMMH may be admixed with the continuous phase in such quantity as will produce the desired electrorheological response.

These quantities may usefully range from 0.05 percent by weight to 20 percent by weight based upon the weight of the ERF. Preferably, the LMMH proportion should be in the range from 0.1 percent by weight to 5 percent by weight and most preferably in the range from 0.5 percent by weight to 2.0 percent by weight.

To produce the electrorheological effect, an electric field is applied to the ERF. For a given ERF composition, the electrorheological response is dependent upon the strength of the applied field. Clearly, however, for ERFs containing different quantities of LMMH or different LMMH compositions or having differing continuous phases, the electrorheological response will vary depending upon these factors. Thus, the selection of an ERF for a particular application requires a selection of LMMH composition, continuous phase composition, LMMH quantity, and electric field strength taking into account environmental factors such as, for instance, the temperature at which the ERF is expected to operate.

The use of aprotic coatings on the LMMHs is beneficial if the results obtained by the use of the LMMH without the aprotic coating is not of the desired magnitude.

Discrete phases (other than LMMRs) useful in the present invention includes any of the particulate compositions normally used in the formulation of ERFs except that in this invention they are free of unbound water. These include, for example, zeolites (synthetic), naturally occurring clays such as, for instance, montmorillonite, faujasite, chabazite and their synthetic analogs. Other useful particulate materials include silicates, alumina, polymers, such as, for instance, polyacrylates, polyacrylate copolymers, cellulose, starch and the like. The previous uses of these materials as the discrete phase has also involved free (unbound) water as an ingredient. In the present invention, which uses the aprotic coating but not unbound water, the ERFs can function at higher temperatures than if water is required as an ingredient.

The present invention ERFs are free of unbound water and include a discrete phase coated, in the case of disperse phases (a) and (c), with a high dielectric constant composition and a continuous phase of a low dielectric constants high dielectric strength fluid. The coating composition is advantageously one that will not boil off under normal conditions of use (i.e., thus is called "heat-stable") but will form an aprotic layer around each particle of the discrete sphase. Thus, the coating composition enhances the particle-particle interaction both in the presence and in the absence of an electric field. This enhancement of particle-particle interaction is dramatically illustrated by the fact that the addition of the high dielectric constant aprotic composition of the present invention significantly increases the viscosity of the ERF over that without the addition. The addition of the high dielectric constant aprotic coating also changes the shape of the shear stress versus shear rate curve for the ERF.

The ERFs of the present invention do not rely upon adsorbed water to provide or produce the electroheological effect and this contributes to their thermal stability. Due to this thermal stability and their powerful electrorheological response, the invention ERFs may be used, for example, in the automotive industry as clutch fluids in self-lubricating clutch systems, as clutch fluids in continuously variable transmissions and in shock absorbers. The ERFs may also find use in vibration or acoustic damping systems to disrupt shock or noise harmonics by continuously varying the "cushioning" properties (viscosity) of the ERF by varying the strength of the applied electric field. Thus, for example, the ERFs could be used as shock dampening nuclear power plant coolant pump mounts in nuclear submarines, shaft bearing mounts for submarines to provide silent, vibration free rotation, absorptive coatings against active sonar, active sound-absorbing partitions, building supports in earthquake-prone areas, etc. The present novel ERFs may also be usefully employed in cushions, mattresses and seats to provide firmer or softer support as and where needed by suitably arranging the applied field in grids to achieve the desired end. Thus, the invention LMMH-based ERFs which combine thermal stability, low solids concentration and strong electrorheological response are useful in a wider range of applications than heretofore possible with previously known ERFs.

The fluids useful as the continuous phase of the present ERFs, using the above-described discrete particles comprise fluids having a relatively low dielectric constant and a high dielectric strength including those which are known to be useful in some prior art electrorheological fluids. These fluids include halocarbon oils, capacitor oils, silicon oils, brake fluids, petroleum distillates, white oils and the like.

The invention ERFs utilize any of a variety of particles coated with a suitable aprotic high boiling, relatively high dielectric constant fluid (hereinafter "coating composition") which will not evaporate under typical operating conditions. The coating compositions of the invention form an electrolyte solution layer analogous to the electric double layer. This coating of an electrolyte solution layer on the particles is stable through a range of temperatures thereby enhancing the electrorheological effect. Further, the invention ERFs show increased suspension stability in that the particulates are less inclined to settle out of ERF mixture.

The dielectric aprotic coating compositions useful in coating the particulates include relatively high dielectric constant, high boiling point (greater than 100° C) compositions such as alkylene carbonates, for example ethylene and propylene carbonate, alkylene sulfones, such as tetramethylene sulfone, ethers, ketones, N-methyl pyrollidone and the like. It is generally preferred that the coating composition have a dielectric constant of greater than 35 and most preferred that the composition have a dielectric constant above 70 with a boiling point above 100° C. The coating composition is partly selected on the basis of having a dielectric constant greater than that of the continuous phase in which it is to be dispersed. If the continuous phase has a dielectric constant as high as 35-40, then the aprotic coating is preferably one having a dielectric constant of 70 or more to get a difference of 30 or more.

The coating composition is added to the particulates in sufficient quantity to form an electrolyte solution layer on the particle surfaces. It is difficult to quantify weight percent ranges for the amount of coating composition to be added to the ERF, considering the various surface areas and porosities of the various particles one can use and also considering the specific gravity of the various coating compositions one can use. However, it is within the skill of practitioners who, having read this disclosure, could find the optimum weight percentages for the given components and avoid putting too much or too little coating composition in mixture. Too much aprotic coating composition can produce too much conductivity in the ERF formulation; too little might leave some particles insufficiently coated to achieve the optimum results.

The ERF may be produced by mixing precoated particles with the continuous phase fluid or it may be produced by adding the particles to a mixture of the continuous phase fluid and the aprotic coating composition. Thus, the invention ERFs including coated particles may be produced by any sequence of mixing steps which allows the coating composition to ultimately coat the surface of the particles. The particulate content of the ERF, using particles other than LMMHs, may vary from 5 to 70 percent by weight depending upon the size and type of particulate, the continuous phase fluid and the coating composition.

In the case of LMMH particulates, these quantities may usefully range from 0.05 percent by weight to 20 percent by weight based upon the weight of the ERF. usually, the particle proportion should be in the range from 0.5 percent by weight to 10 percent by weight, and preferably in the range from 1.0 percent by weight to 5 percent by weight.

Most prior art electrorheological fluid formulations require a dispersant, surfactant or fluidizer to maintain the particulates of the discrete phase in suspension. To the extent that such additives are useful in the present invention, they may be added without significant deleterious effect on the electrical properties of the invention electrorheological fluid compositions.

The advantages of thednvention may be more readily appreciated by reference to the following non-limiting, illustrative examples.

The viscosities of the ERFs of the following sexamples (except Example 10) were measured using an apparatus which included a Brookf ield Model LVF viscometer, a stainless steel cylindrical cup and a Canberra Model 3002 power supply. The positive lead of the power supply was connected to the steel cup. The negative lead of thin steel wire rested upon the shaft of the viscometer so as to provide continuous electrical contact but not to significantly hinder the rotation of the shaft. The viscometer spindle was located in the center of the cup and was completely immersed in the fluid being tested such that the distance from the bottom of the spindle to the bottom of the cup was greater than the distance from the spindle to the side of the cup. The spindle was isolated from the viscometer drive mechanism by a machined plastic sleeve.

The viscosities of the ERFs of Example 10 were measured using an apparatus which included a Brookf ield Model L1"F viscometer, a steel 177.5 ml juice can with the inner epoxy lining removed and a Canberra Model 3002 power supply. The positive lead of the power supply was connected to the steel can. The negative lead of soft copper wire was wrapped around the shaft of the viscometer so as to provide continuous electrical contact but not to significantly hinder the rotation of the shaft. The viscometer spindle was located in the center of the can and was completely immersed in the fluid being tested such that the distance from the bottom of the spindle to the bottom of the can was greater than the distance from the spindle to the side of the can. The spindle wasisolated from the viscometer drive mechanism by a latex rubber sleeve.

Example 1

A quantity of 3 Angstrom (A0) mole sieve zeolite of 3-5 micrometer (0.003-0.005 mm) particle size, purchased from Aldrich Chemical Company, was dried by heating overnight at 600° C with a nitrogen purge. The dried zeolite was then placed in a nitrogen purged glove box where an ERF was prepared. Mineral oil (70 grams) purchased from Aldrich Chemical Company was combined with 30

grams of dried zeolite and the mixture was stirred and shaken to promote homogeneity. The electrorheological behavior for this sample was recorded utilizing the previously described apparatus and the data are reported in Figs. 1 and 2.

Example 2

A 75 gram mixture of ethylene carbonate and mineral oil was heated to 60-70° C in order to melt the ethylene carbonate. The two components showed limited miscibility. The ethylene carbonate and mineral oil mixture was then mixed with zeolite which had been dried as described in Example 1. The final composition had a concentration of 15 percent by weight ethylene carbonate, 30 percent by weight zeolite and 55 percent by weight mineral oil and was very viscous. The composition was diluted with the addition of mineral oil at room temperature to a concentration of 16.83 percent by weight zeolite. The diluted composition was stirred and shaken to promote homogeneity. The composition was then gently heated to 60° C in order to completely distribute the ethylene carbonate. The electrorheological behavior of this sample is also reported in Figs. 1 and 2.

Example 3

A quantity of DRYTECHTM fines (a polyacrylate composition) obtained from The Dow Chemical Company was placed in a nitrogen purged glove box. The DRYTECHTM fines were sieved in the glove box and those particles ssmaller than 212 micrometers (0.212 mm) collected and stored in the glove box. No further pretreatment of the DRYTECHTM fines was undertaken. An ERF was prepared in the nitrogen purged glove box by combining 70 grams of mineral oil, purchased from Aldrich Chemical Co.with 30 grams of the DRYTECHTM fines and the mixture was stirred and shaken to promote' homogeneity. The electrorheological behavior of this sample and similarly prepared samples containing 20 and 40 percent by weight DRYTECHTM polyacrylate in mineral oil are reported in Figs. 3 and 4.

Example 4

Ethylene carbonate (5 grams) was added to 65 gms of mineral oil and the mixture heated to 60-70° C in order to melt the ethylene carbonate. The ethylene carbonate and mineral oil mixture was then mixed with 30 gms of DRYTECHTMfines which had been sieved as described above. The final suspension had a concentration of 5 percent by weight ethylene carbonate, 30 percent by weight DRYTECHTMfines, and 65 percent by weight mineral oil. The suspension was stirred and shaken to promote homogeneity and finally gently heated at 60° C in order to completely distribute the ethylene carbonate. The electrorheological behavior of this sample is also reported in Figs. 3 and 4.

Example 5

A quantity of EF 101 FiberfraxTM fiber (aluminosilicate fiber) obtained from Standard Oil Engineered Materials was dried at 120° C in an oven overnight. The dried material was then placed in a nitrogen purged glove box where the ERF was prepared by combining 95 grams of mineral with 5 grams of EF 101 FiberfraxTM fiber. The mixture was stirred and shaken to spromote homogeneity. The electrorheological behavior of this sample is reported in Figs. 5 and 6.

EXAMPLE 6

94.66 Ethylene carbonate (0.34 grams) was added to grams of mineral oil and the mixture heated to 60-70° C in order to melt the ethylene carbonate. The ethylene carbonate and mineral oil mixture was then mixed with 5 grams of EF 101 fiberfraxTM fiber. The composition had a concentration of 5 percent by weight EF 101 FiberfraxTM fiber, 0.34 percent by weight ethylene carbonate and 94.66 percent by weight mineral oil. The composition was stirred and shaken to promote homogeneity and finally gently heated at 60° C in order to completely distribute the ethylene carbonate. The electrorheological behavior of this sample is also reported in Figs. 5 and 6.

EXAMPLE 7

A quantity of DRYTECHTM fines obtained from The Dow Chemical Company was placed in a nitrogen purged glove box. The DRYTECHTM fines were sieved in the glove box and the particles smaller than 212 micrometers (fines) collected and dried at 50 degrees centigrade for 4 hours under 30 in. (762 mm)Hg vacuum (0.1 MPa). The dried DRYTECHTM fines were then placed back in the glove box where the ERF was prepared by combining 70 grams of mineral oil with 30 grams of dried DRYTECHTM fines. The mixture was stirred and shaken to promote homogeneity. The shear stress versus shear rate electrorheological behavior of this sample is reported in Fig. 7.

Separately, 65 grams of mineral oil was combined with 5 grams of ethylene carbonate and the mixture sheated to 60-70 ° C in order to melt the ethylene carbonate. The ethylene carbonate and mineral oil mixture was then mixed with 30 grams of dried DRYTECH™ fines. The composition was stirred and shaken to promote homogeneity and was noticeably more viscous than the fluid prepared in Example 4. The composition was then gently heated to 60 ° C in order to completely distribute the ethylene carbonate. The final composition had a concentration of 30 percent by weight DRYTECH™ fines, 5 percent by weight (0.057 moles) ethylene carbonate and percent by weight mineral oil. The shear stress versus shear rate electrorheological behavior of this sample is reported in Fig. 8. Note that the viscometer used could not read beyond 700 dynes/cm^2 (0.007 newton/cm^2); consequently, readings recorded as "700 dynes/cm^2" could be substantially higher.

EXAMPLE 8

Mineral oil (63.2 grams) was combined with 6.8 grams of tetramethylene sulfone (TMS) and the mixture heated to 60-70 ° C in order to melt the TMS. The TMS and mineral oil mixture was then mixed with 30 grams of dried DRYTECH™. The composition was stirred and shaken to promote homogeneity and was noticeably more viscous than the fluid prepared in Example 4. The composition was then gently heated to 60 ° C in order to completely distribute the TMS. The final composition had a concentration of 30 percent by weight DRYTECH™ fines, 6.8 percent by weight (0.057 moles) TMS and 63.2 percent by weight mineral oil. The shear stress versus shear rate electrorheological behauior of this sample is reported in Fig. 9.

EXAMPLE 9

The compositions used in Examples 1 (without ethylene carbonate) and 2 (with ethylene carbonate) were allowed to remain undisturbed in capped glass bottles, 6.4 cm in height, at room temperature for a period of 48 hours. The compositions separated into two phases. In the composition not containing ethylene carbonate, the top layer was clear mineral oil while the bottom layer was cloudy and contained the zeolite particles. The composition containing the ethylene carbonate separated to a lesser extent than the other. The clear (mineral oil) layer in the ethylene carbonate composition was only 1.47 cm thick while the same layer in the composition which did not contain any ethylene carbonate was 2.54 cm thick. This indicates that the ethylene carbonate-containing composition is more stable and settles to a lesser degree than the composition not containing ethylene carbonate.

EXAMPLE 10

An alkoxide gel was prepared by mixing magnesium ethoxide and aluminum ethoxide in dry methanol under moisture free conditions with subsequent water addition to produce an alkoxide-based LMMH gel. This provided a $Mg_{1.7}Al_{0.5}(OH)_5$ compound, as described before, which was relatively viscous at room temperature even though the concentration of the LMMH was only 1 percent by weight.

An ERF was prepared by admixing 45.06 g of this alkoxide LMMH gel containing 1 percent LMMH with 138.89 g of anhydrous methanol. This produced a composition containing 0.45 g LMMH or 2450 ppmw.

The composition was placed in the apparatus described above and the viscosity measured at field strengths of 0, 10, 100 150, and 200 applied volts. Ten measurements were taken at each voltage level with a 20 second interval between measurements. Upon stepping up the field strength, the voltage and viscosity were allowed to equilibrate for 2-3 minutes before readings were taken at approximately 20 second intervals. To test the effect of current direction, the polarity was reversed at the 10 volt level. This reversal produced no significant change in the measured viscosity. The results are shown in Figure 10.

EXAMPLE 11

A solution containing 3.0 g (0.004 moles) of the chloride salt of a monoquaternary amine (ARQUAD™ 2HT-75, Akzo Chemie America, 75 percent active) was prepared by dissolving the salt in a mixture of water (9 g), methanol (5 g), and isopropanol (4 g). A synthetic clay, LAPONITE RDS™ (Laporte Industries Ltd.) which contains 6.0 percent pyrophosphate was then added to the amine solution and the resulting mixture was blended under high shear. The solvent was then removed by vacuum and residual solids were filtered and washed with distilled water. The washed solids (4.7 g) were dried and then mixed into mineral oil (55.4 g) at high shear for two minutes and thereafter shaken for 30 minutes. Upon testing this mixture, which contained 7.8 percent by weight solids based on the total weight of solids and oils, in an electric field, it showed no electrorheological response aver the field strengths examined.

The LAPONITE-amine-mineral oil mixture (60.1 g) was then blended at high shear with 50 g of $Mg_xAl_y(OH)_z$ LMMH gel (1.35 percent by weight LMMH in methanol) to produce a milky fluid. The milky fluid was subjected to evaporation to remove the methanol. This resulted in a yellow, low viscosity mixture. The electrorheological response of this mixture at shear rates of 0.105 sec^{-1} and 21 sec^{-1} is shown in Figure 11.

EXAMPLE 12

A clear solution containing 2.5 g (0.0088 moles) of stearic acid in acetone (40 g) was prepared. To this solution was added 90.1 g of LMMH gel (1.33 percent by weight LMMH in methanol) and the resultant mixture was thoroughly agitated. The solvents were then removed by vacuum and 3.91 g of white solids were recovered. The solids were dried at 120° C for one hour yielding 3.66 g of dry white solids. After grinding, 3.4 g of solids were recovered, added to 56.6 g of mineral oil and blended under high shear for two minutes. Some solids were observed to settle out after 30 minutes. The electrorheological response of this mixture at shear rates of 0.105 sec-1 and 21 sec-1 is shown in Figure 12.

EXAMPLE 13 (for comparison with Examples 11, 12, & 14)

A solution of 5.12 g of (0.10 moles) of LAPONITE RDS™ in 100 cc of deionized water was prepared. A second solution was prepared containing 7.5 g (0.010 moles) of 75 percent active ARQUAD™ 2HT-75 dissolved in 400 g of isopropanol. These two solutions were mixed together and the solvents removed by vacuum to recover 11.15 g of solids. The recovered solids were dried at 120° C for 30 minutes and ground. The ground solids were then washed with one liter of deionized water and again dried at 120° C for one hour yielding 10.4 g of white powder. The powder was dissolved in an isopropanol (400 g)-water (50 g) mixture to which 52 g of mineral oil swere added. Removal of the solvent resulted in the formation of 61.37 g of an almost-clear, thick, creamy gel. An additional 152 g of mineral oil was added to reduce the sample viscosity so that electrorheological readings could be taken. The final product contained 2.3 percent by weight LAPONITE RDS, 2.54 percent by weight ARQUAD™ 2HT-75, and 95.15 percent by weight mineral oil, based upon the total product weight. The electrorheological response of this product at shear rates of 0.105 sec-1 and 21 sec^{-1} is shown in Figure 13.

EXAMPLE 14

A mixture was prepared by adding 58.3 g (0.005 moles) of LMMH gel (1.17 percent by weight LMMH in methanol) to 58 g of mineral oil. The mixture was blended for 30 minutes under high shear. To this mixture, with stirring, was added 1.42 g (0.005 moles) of stearic acid dissolved in methanol. The solvent was removed under vacuum resulting in 58.9 g of clear, thick gel being recovered. An additional 60.0 g of oil was added and the mixture blended at high shear for two minutes in order to reduce the viscosity enough for the ER response to be measured. The final composition of the sample was 0.57 percent LMMH, 1.18 percent by weight stearic acid, 98.25 percent by weight mineral oil. The electrorheological response at shear rates of 0.105 sec^{-1} and 21 sec^{-1} is shown in Figure 14.

The results demonstrate that LMMH with stearic acid (Examples 12 and 14) has a better electrorheological response than LAPONITE™(s) and ARQUAO™ 2HT-75 (Example 13) but not as good as the response of LMMH with LAPONITE™ and ARQUAD™ 2HT-75 (Example 11).

Claims

1. An electrorheological fluid comprising a continuous phase having uniformly dispersed therein a discrete phase, characterized in that the continuous phase comprises a dielectric carrier fluid having a relatively low dielectric constant and in that the discrete phase is at least one of:

(a) a discrete phase comprising non-conductive fine particles coated with a dielectric aprotic coating composition having a relatively high dielectric constant; or

(b) a discrete phase comprising crystalline layered mixed metal hydroxide; or

(c) a discrete phase comprising crystalline layered mixed metal hydroxide coated with said aprotic coating composition,

wherein the crystalline layered mixed metal hydroxide of (b) and (c) is at least one crystalline layered mixed metal hydroxide of the general formula:

$Li_mD_dT(OH)_{(m+2d+3+na)}(A^n)a$

wherein:

m is 0 to 1;

D is a divalent metal ion selected from Mg, Ca, Ba, Sr, Mn, Fe, Co, Hi, Cu, and Zn;

d is 0 to 4;

T is a trivalent metal ion selected from Al, Ga,

Or, and Fe;
A is a polyvalent or monovalent anion other than an hydroxyl ion;
n is the valence of the anion A;
a is the number of anions A in the formula;
m + d is greater than 0; and
(m + 2d + 3 + na) is equal to or greater than 3.

2. An electrorheological fluid as claimed in Claim 1 comprising discrete phase (b) and/or (c), wherein said crystalline layered mixed metal hydroxide has the formula:
$Mg_xAl_y(OH)_z$ wherein:
x is on the average 1.7;
y is on the average 0.5; and
z is on the average 5.

3. An electrorheological fluid as claimed in Claim 1 comprising discrete phase (b) and/or (c), wherein:
m is 0 or 0.5 to 0.75;
D is Mg or Ca;
d is 1 to 3; and
T is Al or Fe.

4. An electrorheological fluid as claimed in any one of the preceding claims comprising disperse phase (b) or (c), further comprising an amount of a functionalizer sufficient to aid dispersing of the layered mixed metal hydroxide in the continuous phase.

5. An electrorheological fluid as claimed in Claim 4, wherein said functionalizer is an aliphatic carboxylic acid.

6. An electrorheological fluid as claimed in Claim 5, wherein said aliphatic carboxylic acid is stearic acid.

7. An electrorheological fluid as claimed in any one of 5claims 1 to 3, comprising disperse phase (b) and/or (c), wherein the layered mixed metal hydroxide is complexed with a dispersible negatively-charged functionalizing species.

8. An electrorheological fluid as claimed in Claim 7, wherein said functionalizing species is the reaction product of a synthetic clay and an amine salt.

9. An electrorheological fluid as claimed in any one of the preceding claims comprising discrete phase (b) and/or (c), wherein the layered mixed metal hydroxide is present in an amount of 0.1 to 5 percent by weight.

10. An electrorheological fluid as claimed in any one of the preceding claims comprising discrete phase (a), wherein the non-conductive particles comprise clays, silicates, aluminas, zeolites, polyacrylates, polyacrylate copolymers, cellulose, starch, or mixtures thereof.

11. An electrorheological fluid as claimed in Claim 10, wherein said disperse phase (a) particles are present in an amount of 5 to 70 percent by weight.

12. An electrorheological fluid as claimed in any one of the preceding claims comprising discrete phase (a) and/or (c), wherein the aprotic coating composition is selected from ethers, ketones, alkylene carbonates, alkylene sulfones, and N-methyl pyrrolidone.

13. An electrorheological fluid as claimed in Claim 12, wherein the particles comprise layered mixed metal hydroxide or zeolites; the continuous phase is mineral or silicone-base oil; and the aprotic coating composition is ethylene carbonate.

14. An electrorheological fluid as claimed in any one of sthe preceding claims, wherein the continuous phase is selected from alcohols, polyols, polyglycols, hydrocarbons, halogenated hydrocarbons, mineral oils, silicone-based oils and greases, ethers, aldehydes and ketones.

15. An electrorheological fluid as claimed in any one of the preceding claims, wherein the dielectric constant of the continuous phase is not more than 40 and the dielectric constant of the aprotic coating composition is greater than the dielectric constant of the continuous phase by a difference of at least 30.

16. An electrorheological fluid as claimed in Claim 15, wherein the dielectric constant of the continuous phase is less than 35.

17. An electrorheological fluid as claimed in Claim 16, wherein the dielectric constant of the continuous phase is less than 5.

18. A method of making a fluid which has an electrorheological response upon application thereto of an electric field, said method comprising:

(1) providing a continuous phase of dielectric fluid having a relatively low dielectric constant:

(2) dispersing in the continuous phase, as a discrete phase,

(a) fine particles of a dielectric solid, said particles bearing a coating of a dielectric aprotic material having a relatively high dielectric constant,

(b) fine particles of crystalline layered mixed metal hydroxide, and/or

(c) fine particles of crystalline layered mixed metal hydroxide as in (b) above and which bear a coating of a dielectric aprotic material as described in (a) above, said particles being in an amount sufficient to impart electrorheological response to the application thereto of an electric field,

said crystalline layered mixed metal hydroxide of (b) and (c) being at least one compound of the general formula:
$Li_mD_dT(OH)_{(m+2d+3+na)}(A^n)_a$ wherein:
m is 0 to 1;
D is a divalent metal ion selected from Mg, Ca, Ba, Sr, Mn, Fe, Co, Ni, Cu, and Zn;
d is 0 to 4;
T is a trivalent metal ion selected from Al, Ga, Or, and Fe;
A is a polyvalent or monovalent anion other than an OH ion;

n is the valence of the anion A;

a is the number of anions A in the formula;

m + d is greater than zero; and

(m + 2d + 3 + na) is equal to or greater than 3.

19. A method as claimed in Claim 18, wherein the continuous phase and/or the dispersed phase is as defined in any one of Claims 2 to 17.

20. The use of an electrorheological fluid as defined in any one of Claims 1 to 17 in an electrorheological device.

21. An electrorheological device comprising an electrorheological fluid characterized in that said fluid is as defined in any one of Claims 1 to 17.

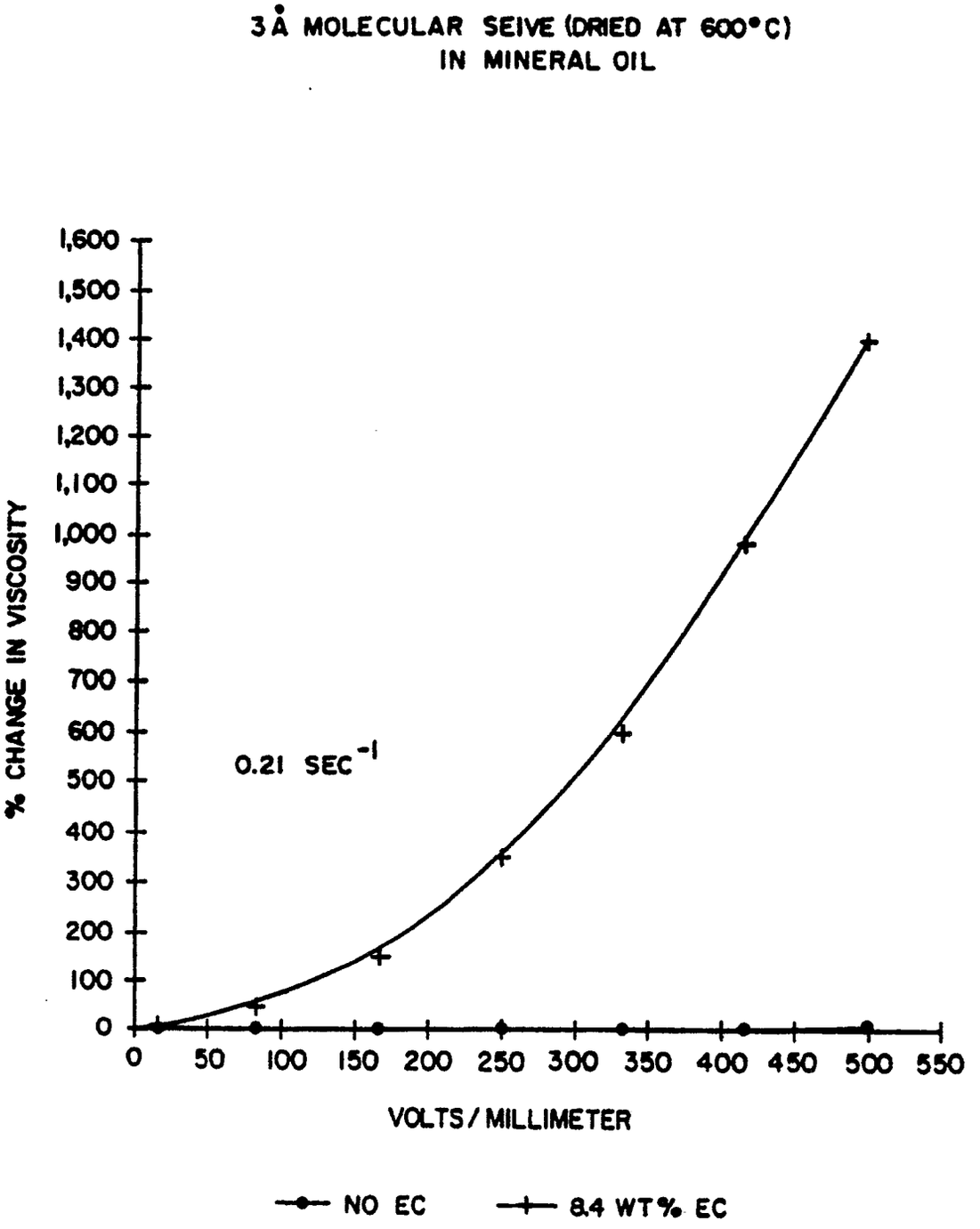
3 Å MOLECULAR SEIVE (DRIED AT 600°C)
IN MINERAL OIL
% CHANGE IN VISCOSITY
1,600
1,500
1,400
1,300
1,200
1,100
1,000
900
800
700
600
500
400
300
200
100
0
0.21 SEC-1
0
50
100
150
200
250
300
350
400
450
500
550
VOLTS / MILLIMETER
NO EC
8.4 WT% EC

FIG.1

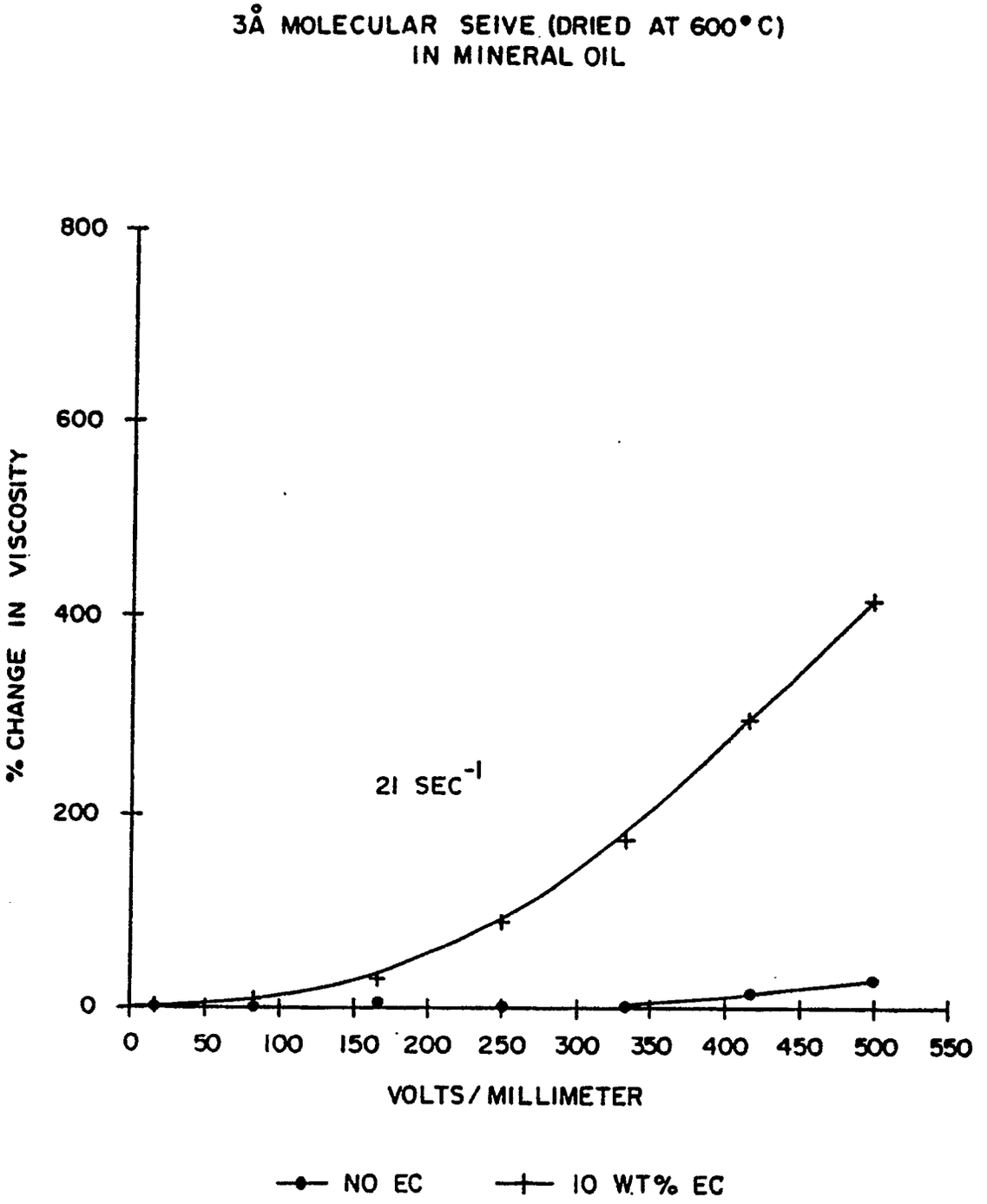
3Å MOLECULAR SEIVE (DRIED AT 600°C)
IN MINERAL OIL
% CHANGE IN VISCOSITY
800
600
400
200
0
21 SEC-1
0
50
100
150
200
250
300
350
400
450
500
550
VOLTS/MILLIMETER
NO EC
10 WT% EC

FIG.2

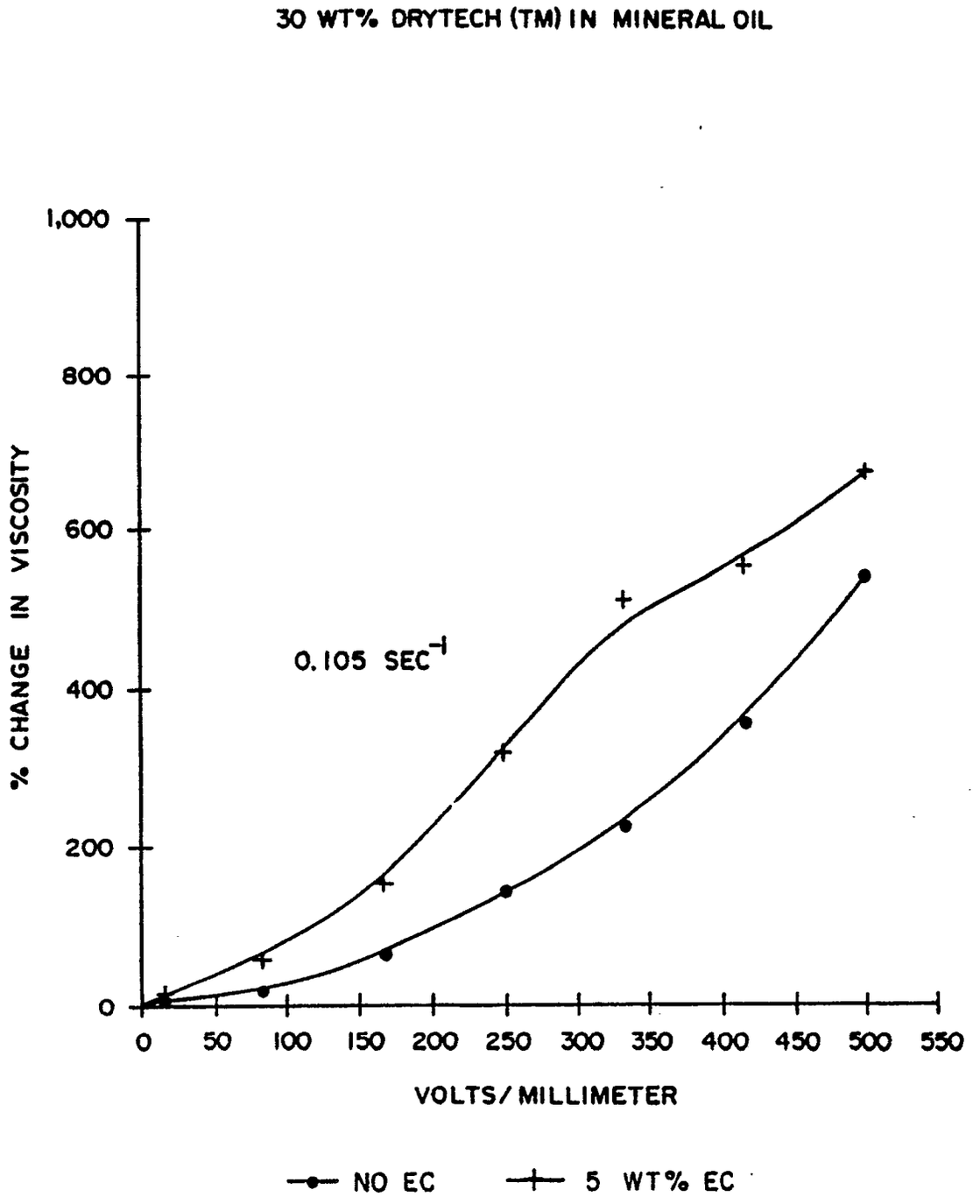
30 WT% DRYTECH (TM) IN MINERAL OIL
% CHANGE IN VISCOSITY
1,000
800
600
400
200
0
0.105 SEC⁻¹
0
50
100
150
200
250
300
350
400
450
500
550
VOLTS/MILLIMETER
NO EC
5 WT% EC

FIG.3

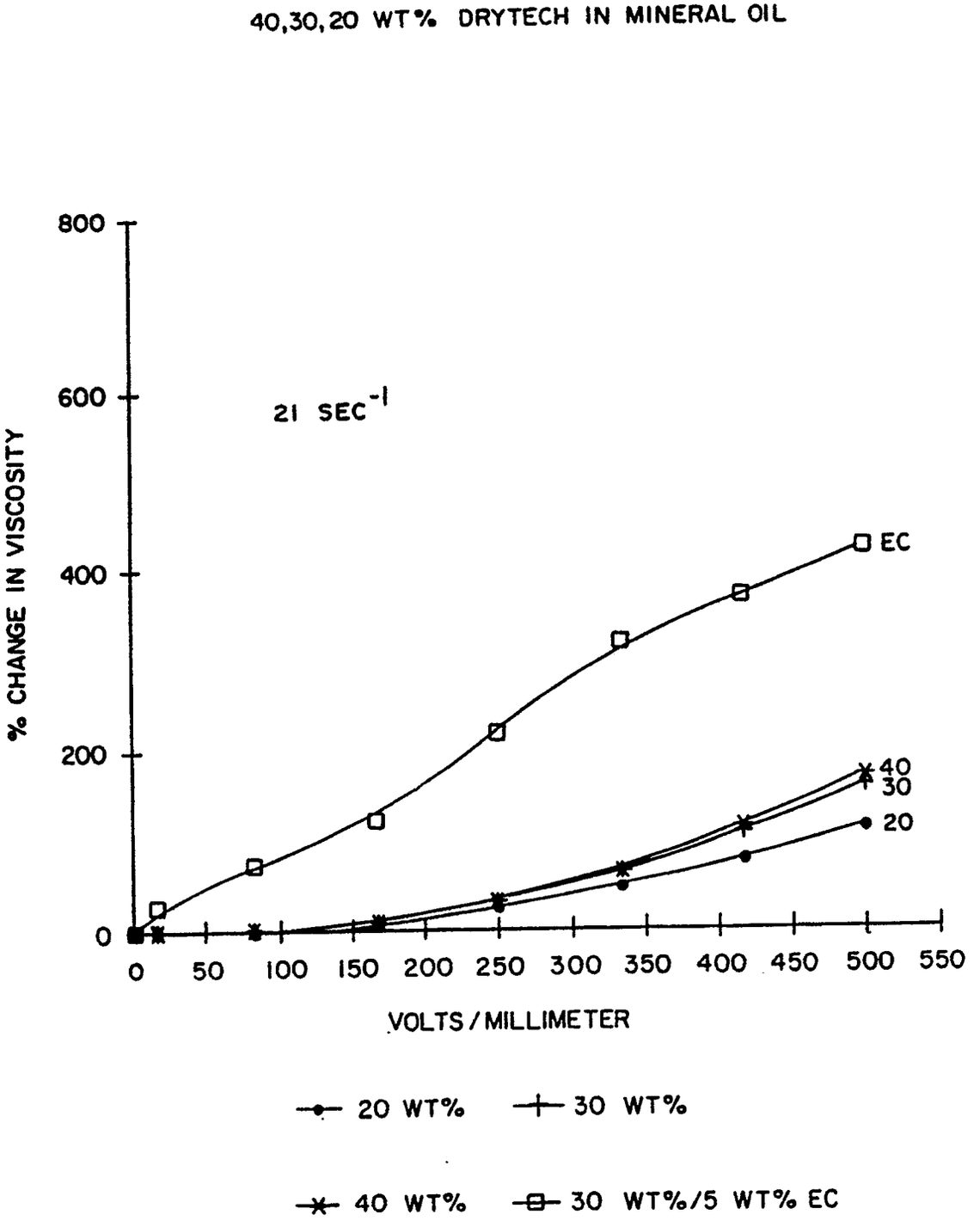
40,30,20 WT% DRYTECH IN MINERAL OIL
% CHANGE IN VISCOSITY
800
600
400
200
0
21 SEC-1
EC
40
30
20
0
50
100
150
200
250
300
350
400
450
500
550
VOLTS/MILLIMETER
20 WT%
30 WT%
40 WT%
30 WT%/5 WT% EC

FIG.4

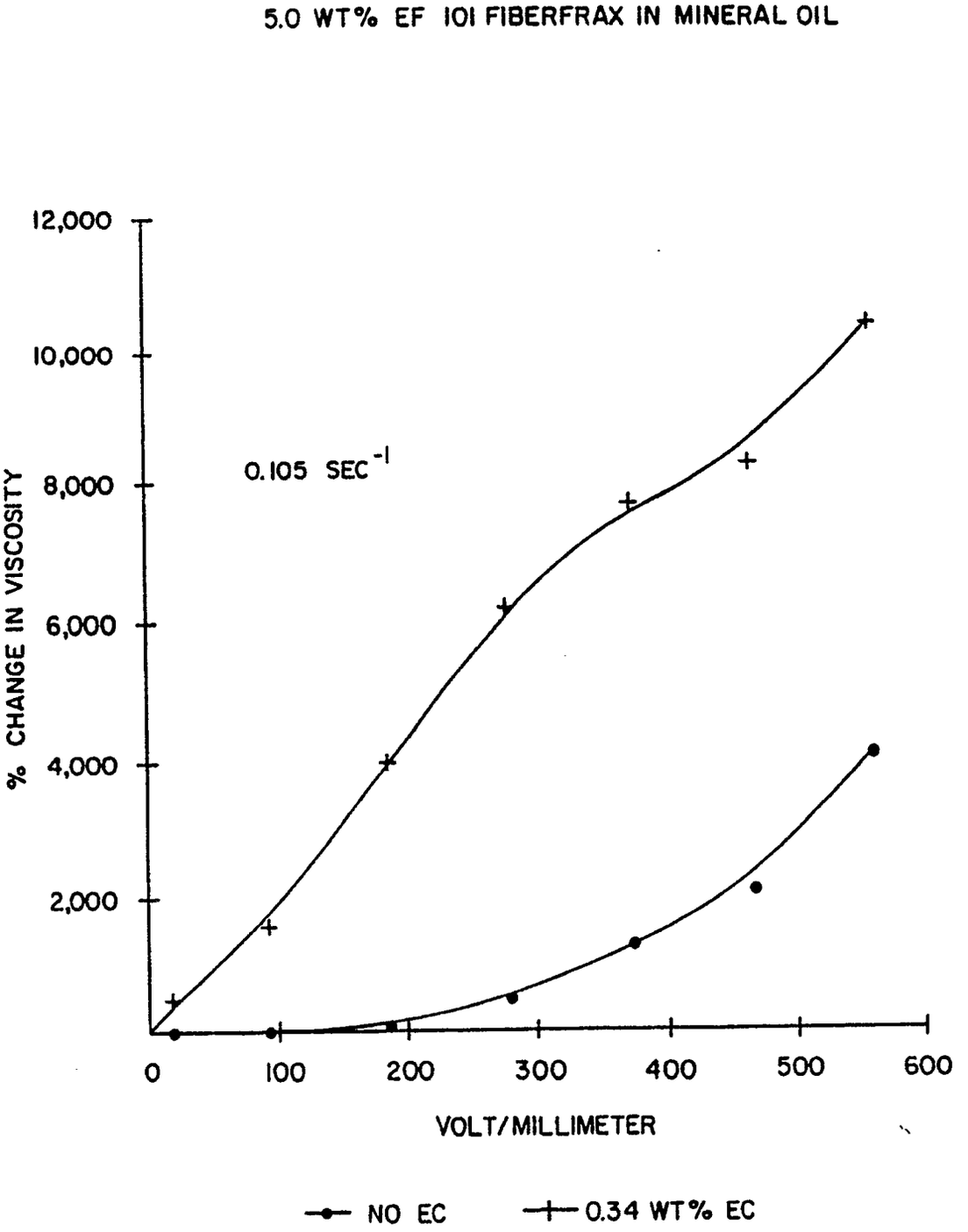
5.0 WT% EF 101 FIBERFRAX IN MINERAL OIL
12,000
10,000
8,000
6,000
4,000
2,000
% CHANGE IN VISCOSITY
0.105 SEC-1
0
100
200
300
400
500
600
VOLT/MILLIMETER
NO EC
0.34 WT% EC

FIG.5

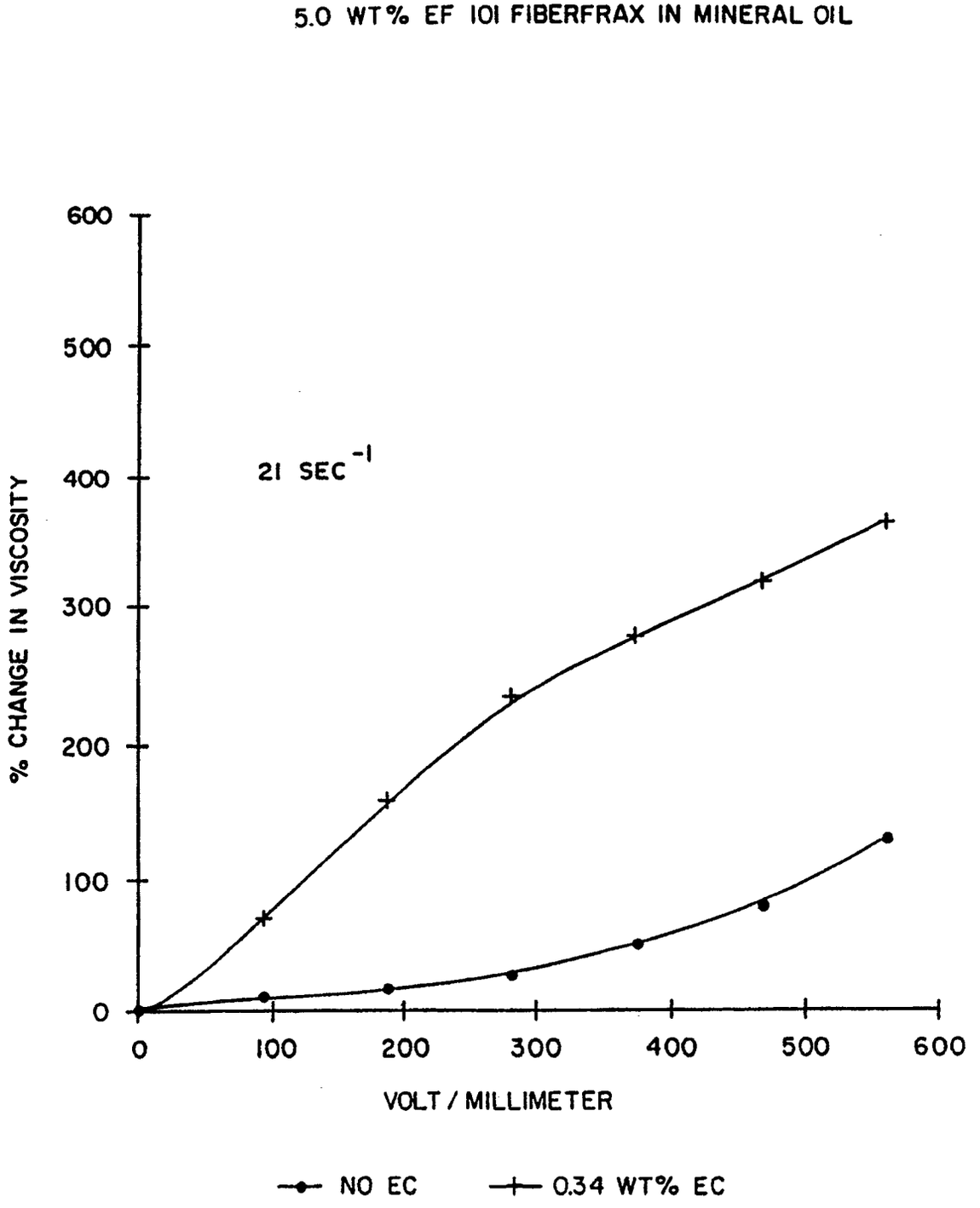
5.0 WT% EF 101 FIBERFRAX IN MINERAL OIL
% CHANGE IN VISCOSITY
600
500
400
300
200
100
0
21 SEC -1
0
100
200
300
400
500
600
VOLT / MILLIMETER
NO EC
0.34 WT% EC

FIG. 6

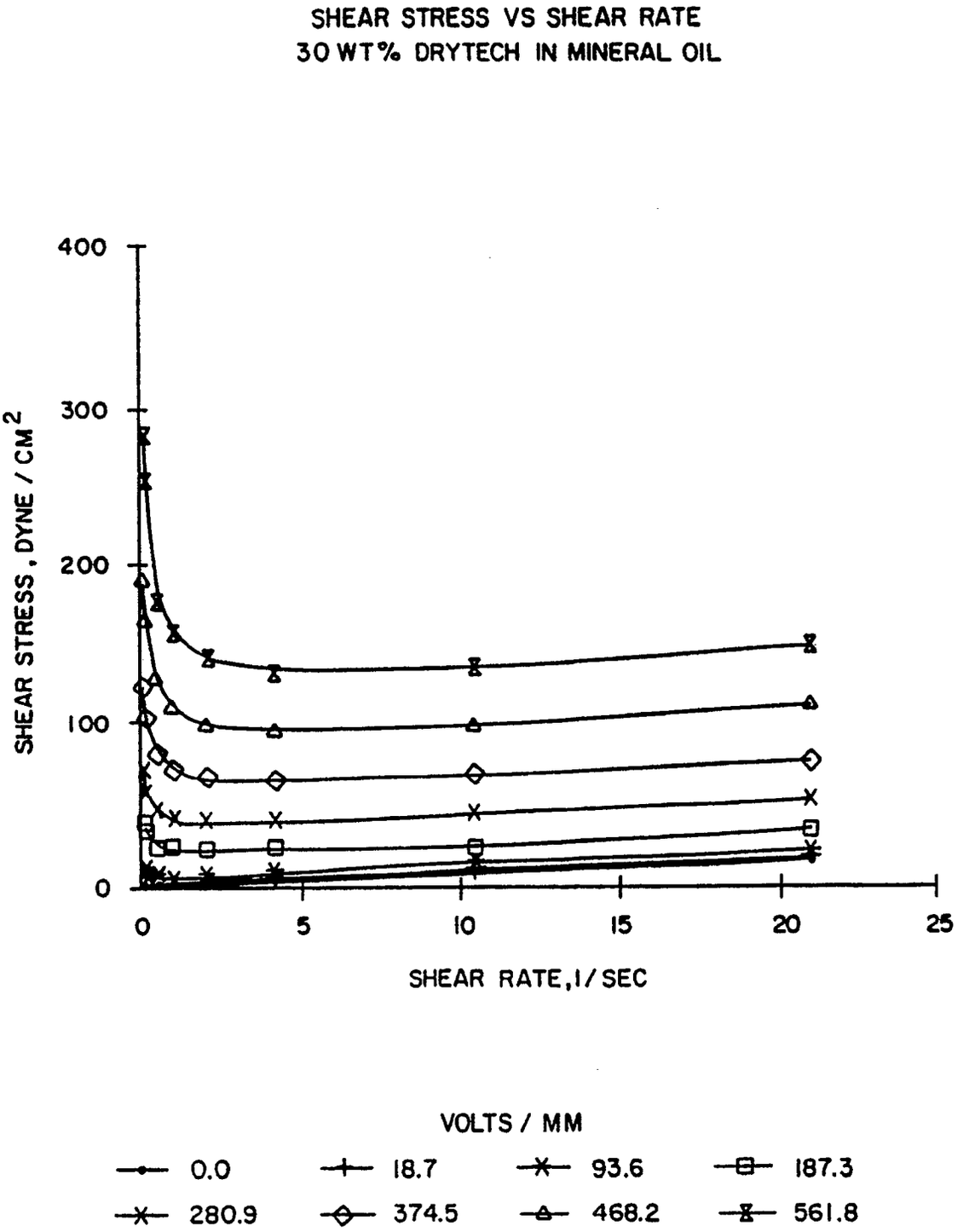
SHEAR STRESS VS SHEAR RATE
30 WT% DRYTECH IN MINERAL OIL
SHEAR STRESS, DYNE / CM 2
400
300
200
100
0
0
5
10
15
20
25
SHEAR RATE, 1/SEC
VOLTS / MM
0.0
18.7
93.6
187.3
280.9
374.5
468.2
561.8

FIG.7

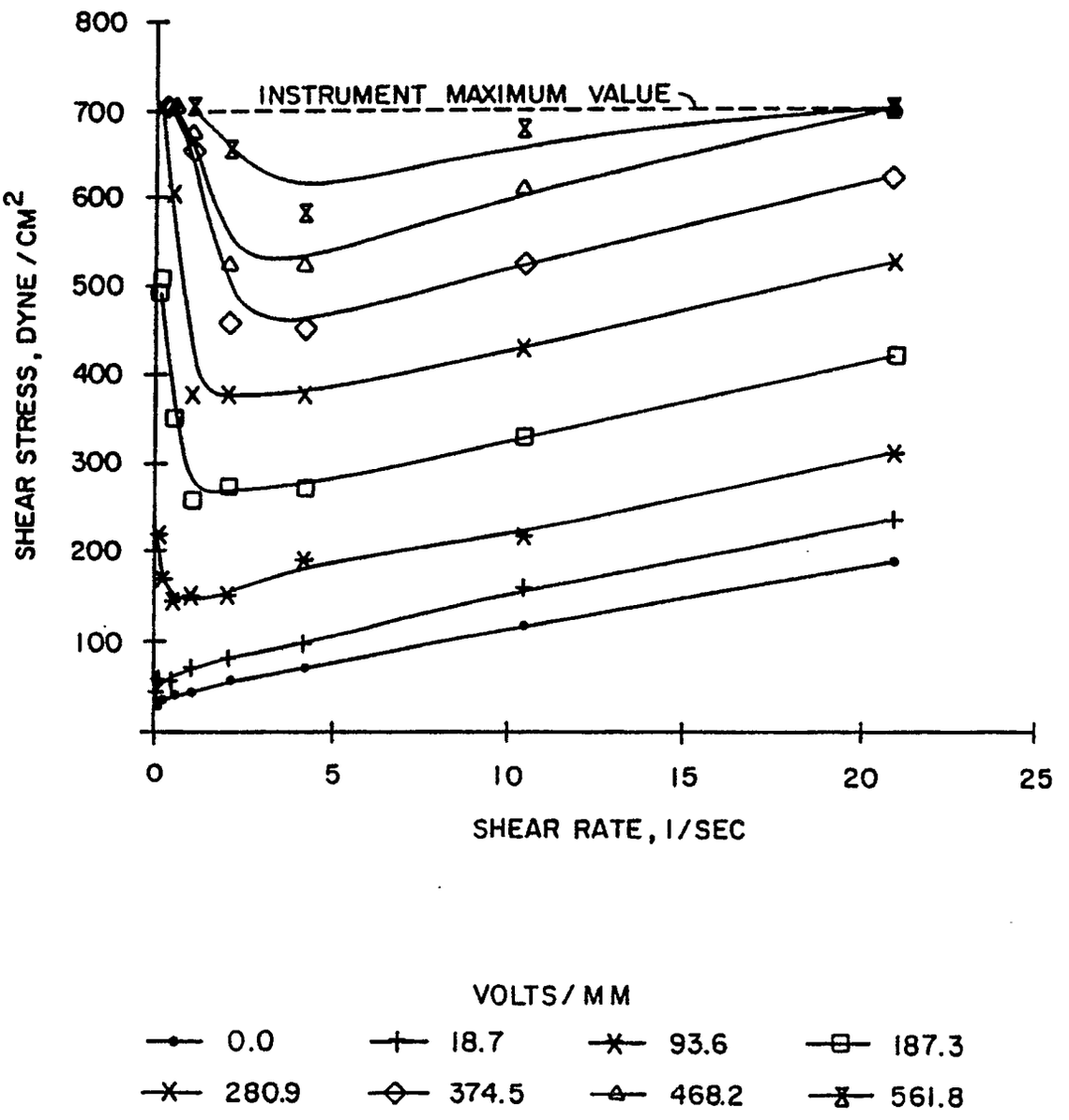
SHEAR STRESS VS SHEAR RATE
30 WT% DRYTECH + 5 WT% EC IN MINERAL OIL
INSTRUMENT MAXIMUM VALUE
SHEAR STRESS, DYNE / CM2
800
700
600
500
400
300
200
100
0
5
10
15
20
25
SHEAR RATE, 1/SEC
VOLTS / MM
0.0
18.7
93.6
187.3
280.9
374.5
468.2
561.8

FIG.8

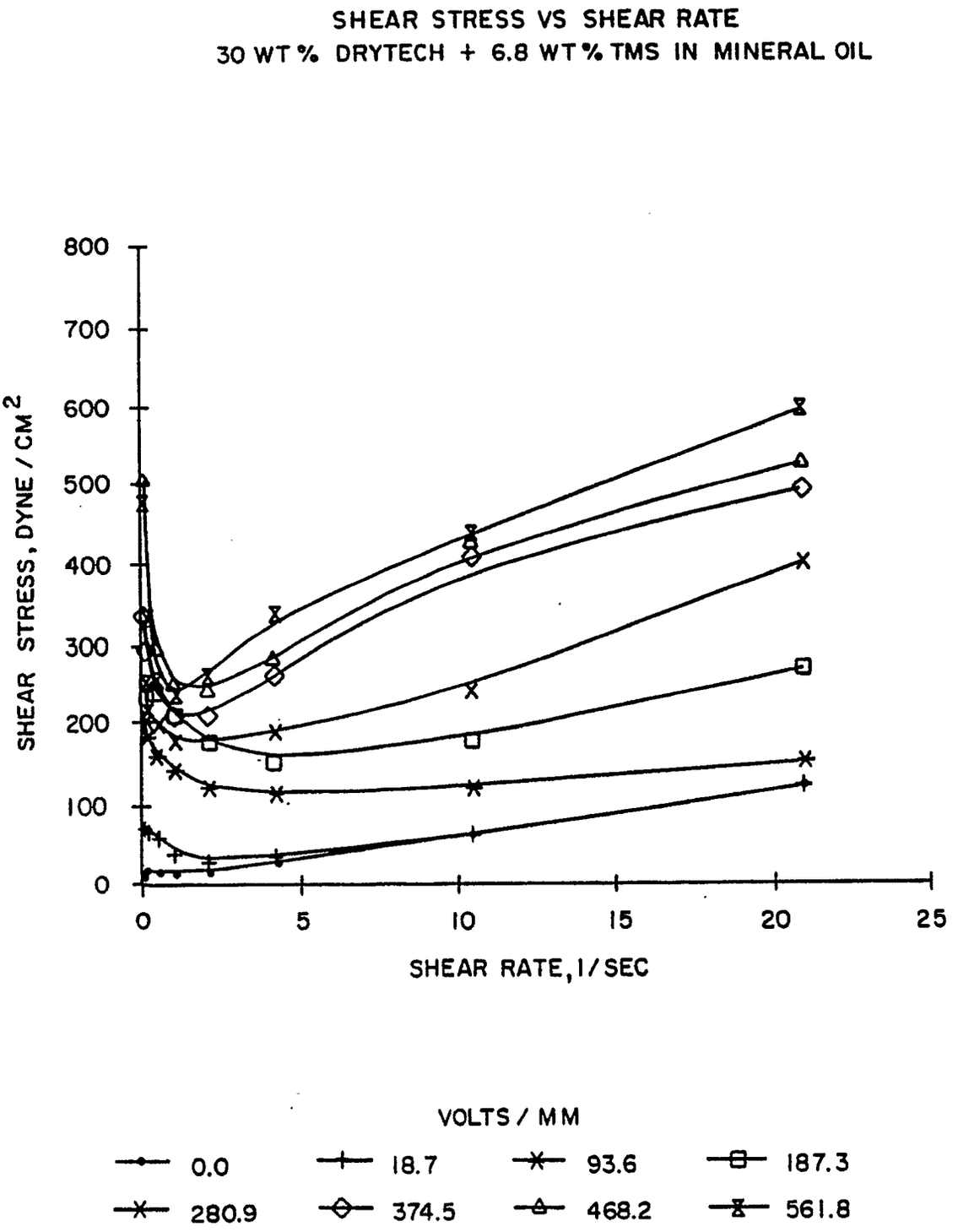
SHEAR STRESS VS SHEAR RATE
30 WT % DRYTECH + 6.8 WT % TMS IN MINERAL OIL
SHEAR STRESS, DYNE / CM 2
800
700
600
500
400
300
200
100
0
0
5
10
15
20
25
SHEAR RATE, 1/SEC
VOLTS / MM
0.0
18.7
93.6
187.3
280.9
374.5
468.2
561.8

FIG.9

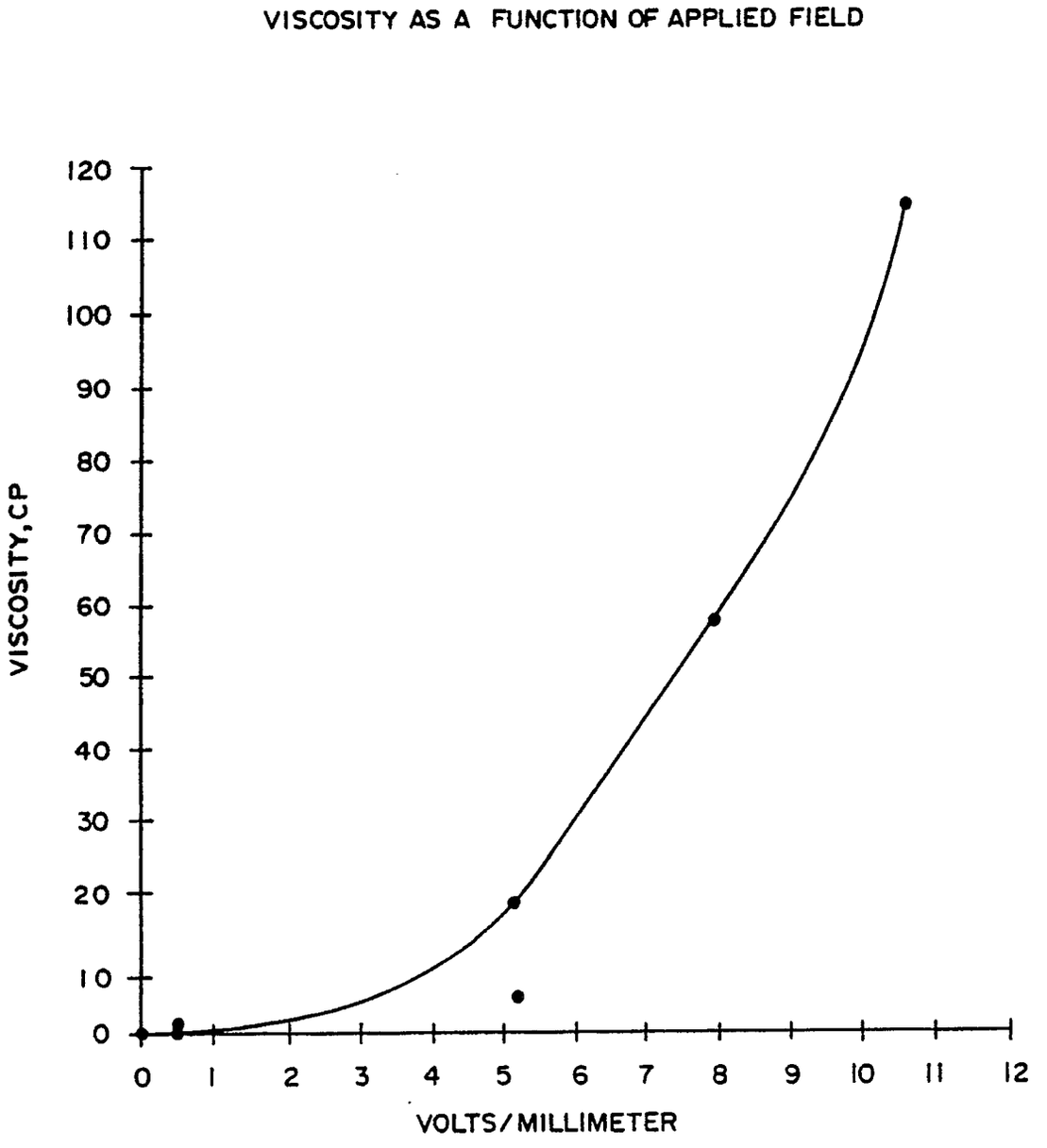
VISCOSITY AS A FUNCTION OF APPLIED FIELD
VISCOSITY, CP
120
110
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
11
12
VOLTS/MILLIMETER

FIG.10

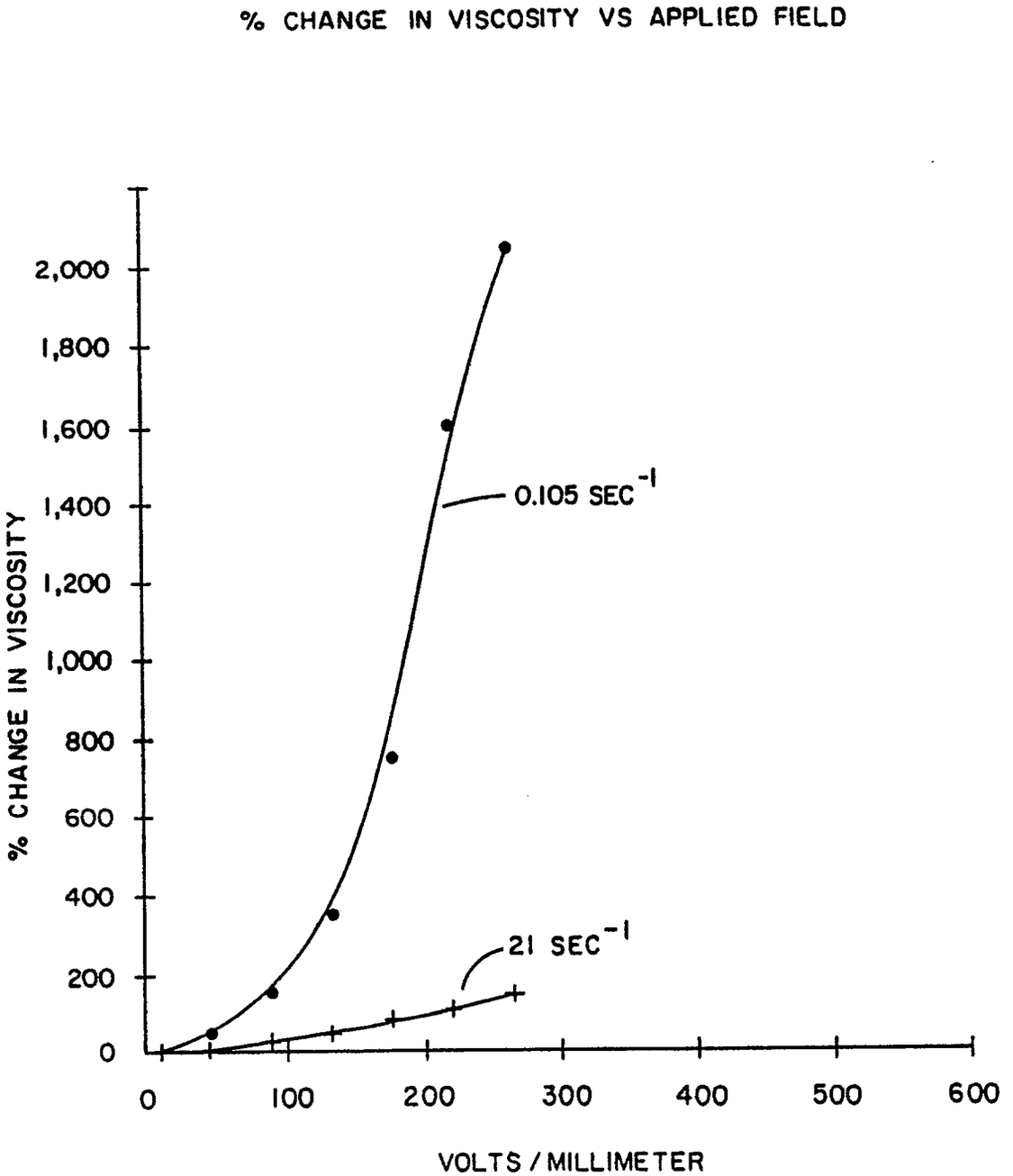
% CHANGE IN VISCOSITY VS APPLIED FIELD
% CHANGE IN VISCOSITY
2,000
1,800
1,600
1,400
1,200
1,000
800
600
400
200
0
0.105 SEC-1
21 SEC-1
0
100
200
300
400
500
600
VOLTS / MILLIMETER

FIG.11

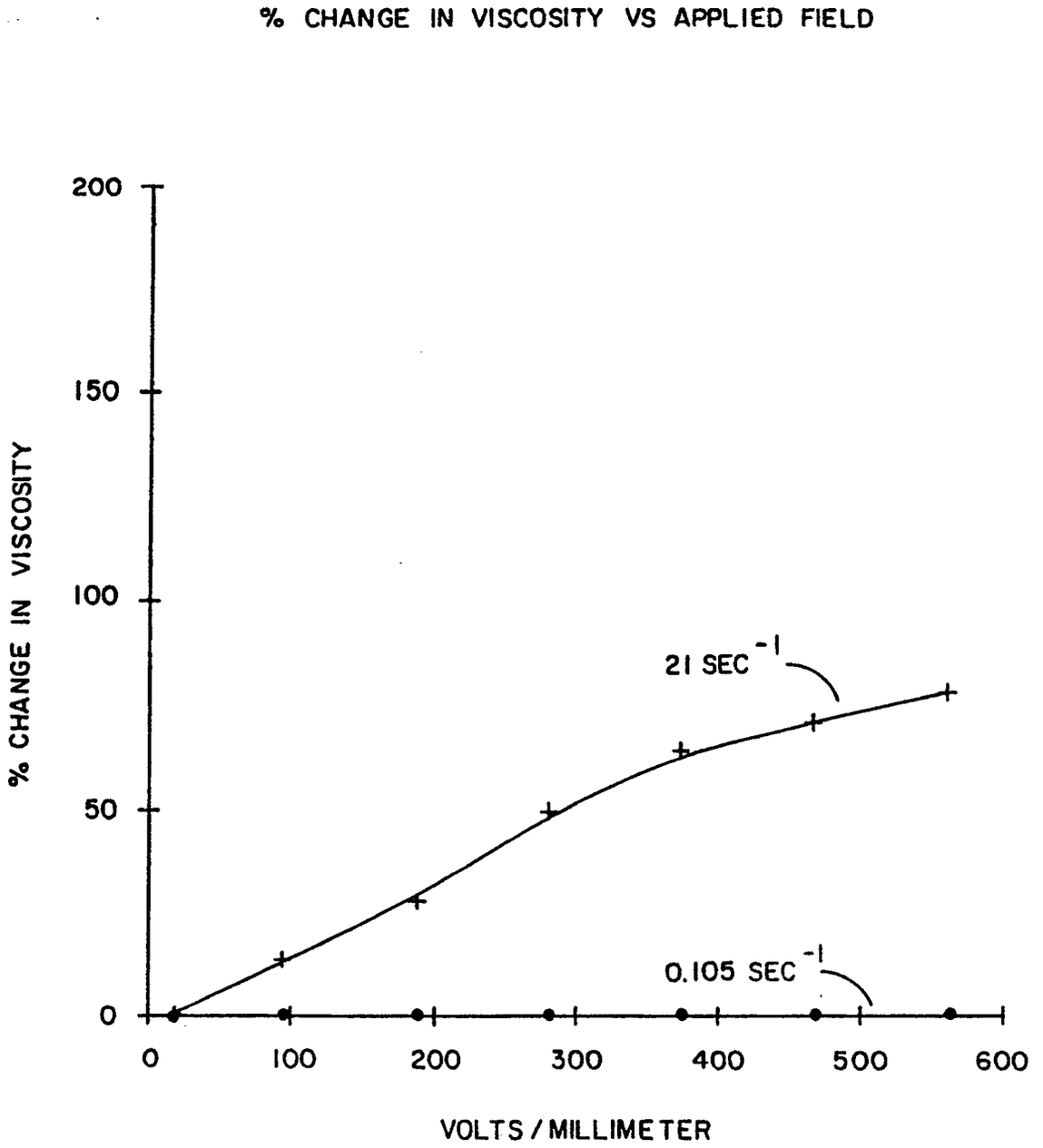
% CHANGE IN VISCOSITY VS APPLIED FIELD
200
150
100
50
0
% CHANGE IN VISCOSITY
21 SEC -1
0.105 SEC -1
0
100
200
300
400
500
600
VOLTS / MILLIMETER

FIG.12

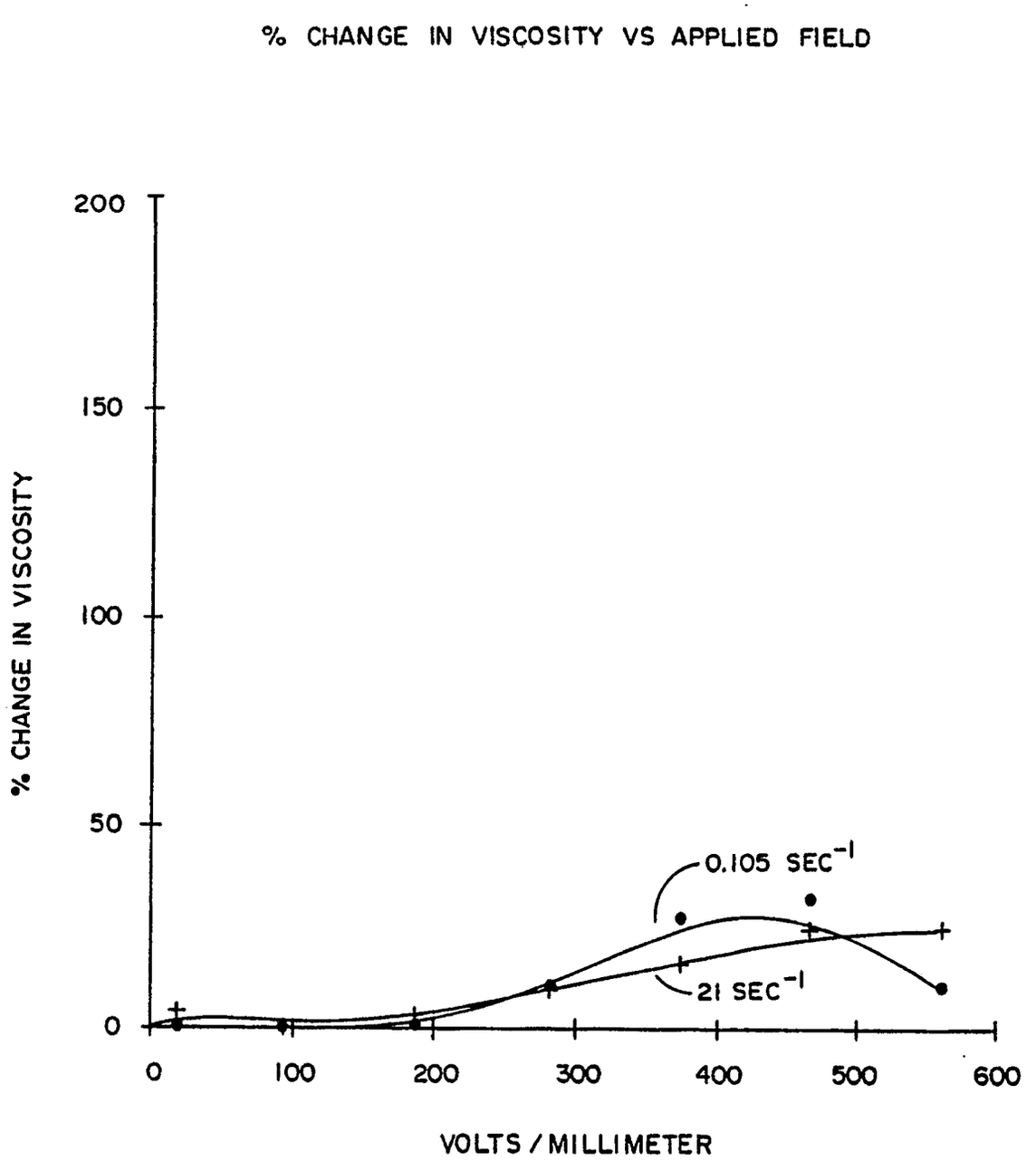
% CHANGE IN VISCOSITY VS APPLIED FIELD
200
150
100
50
0
% CHANGE IN VISCOSITY
0.105 SEC-1
21 SEC-1
0
100
200
300
400
500
600
VOLTS / MILLIMETER

FIG.13

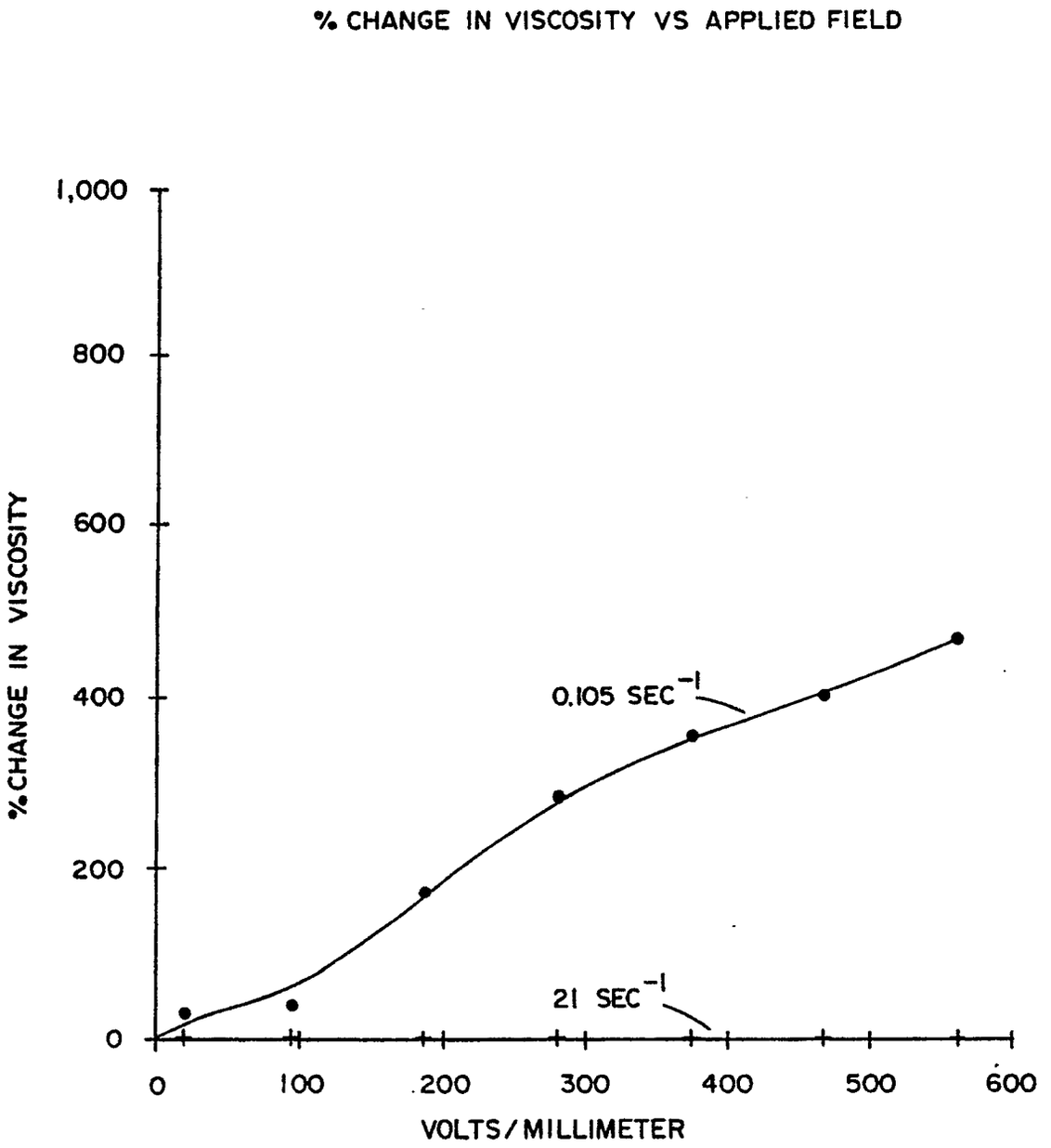
% CHANGE IN VISCOSITY VS APPLIED FIELD
1,000
800
600
400
200
0
% CHANGE IN VISCOSITY
0.105 SEC⁻¹
21 SEC⁻¹
0
100
200
300
400
500
600
VOLTS/MILLIMETER

FIG.14

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2150

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)
A	US-A-3 427 247 (R.L. PECK) * Claims 1,5,7 *	1,4,5,10, 11,12,14, 18-21	C 10 M 171/00
A	EP-A-0 313 351 (THE BOARD OF REGENTS ACTING FOR AND ON BEHALF OF THE UNIVERSITY OF MICHIGAN) * Claims 1-16 *	1,10, 18-21	
D,A	EP-A-0 207 811 (THE DOW CHEMICAL CO.) * Claims 1-13 *	1,2,14,18	
P,X	EP-A-0 374 525 (BRIDGESTONE) * Claims 1-9; page 3, line 40 - page 4, line 22 *	1,10-21	
P,X	PATENT ABSTRACTS OF JAPAN, vol. 14, no. 176 (C-707)[4119], 9th April 1990; & JP-A-2 26 634 (TOYODA GOSEI CO., LTD) 29-01-1990	1,2,3,11, 14,18-21	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	07 February 91	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
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E: earlier patent document, but published on, or after the filing date
D: document oited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document