

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 311 984
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88116871.0

(51) Int. Cl.4: **C10M 107/50 , C10M 169/04**

(22) Date of filing: 11.10.88

**C08L 83/08 , //(C10M169/04,
107:50,125:26,145:14,145:40),
C10N20:06,C10N40:14**

(30) Priority: 12.10.87 GB 8723924

(43) Date of publication of application:
19.04.89 Bulletin 89/16

(84) Designated Contracting States:
AT BE CH DE ES FR GR IT LI LU NL SE

(71) Applicant: **AMERICAN CYANAMID COMPANY**
1937 West Main Street P.O. Box 60
Stamford Connecticut 06904-0060(US)

(72) Inventor: **Brooks, Douglas Alan**
31 Greville Road
London E17 9HG(GB)
Inventor: **Kandian, Sivakumar**
59 New Road
East Molesey Surrey KT8 9PX(GB)

(74) Representative: **Wächtershäuser, Günter, Dr.**
Tal 29
D-8000 München 2(DE)

(54) **Improvements in or relating to electro-rheological fluids.**

(57) An electro-rheological fluid comprises a solid phase dispersed in a base liquid comprising a polyfluoroalkyl-methyl siloxane.

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IMPROVEMENTS IN OR RELATING TO ELECTRO-RHEOLOGICAL FLUIDS

This invention relates to improved electrorheological fluids.

Electro-rheological (ER) fluids, also sometimes termed electroviscous (EV) fluids, consist of finely divided solid particles suspended in a non-conducting base liquid. Normally the flow characteristics of an ER fluid are Newtonian, ie they behave as a conventional hydraulic fluid, but when an electric field is applied across the fluid, its behaviour changes and no flow can occur until a particular shear stress, whose magnitude depends on the applied voltage, is reached. This rheological effect is reversible upon removal of the applied field. Because of these remarkable rheological properties, permitting the transmission of stress under an applied field, ER fluids are being increasingly used in various fluid power systems and engineering applications, for example in clutches, brake systems, fluid drives and couplings, as well as in other devices.

The currently preferred ER fluids in commerce are based on the teachings of GB-A-1570234, and comprise the lithium salt of polymethacrylic acid (LMAA) as the solid phase in a base liquid of a chlorinated paraffin. Although these ER fluids have been moderately successful, they are nonetheless deficient in a number of properties. For example, their no-field viscosity is relatively high, which in some instances can make it difficult to control the fluid. Also, they have a relatively high pour-point, resulting in an undesirably high viscosity at low temperatures, whilst on the other hand at high temperatures they start to break down to hydrochloric acid, which of course is highly corrosive. In consequence, the useful temperature range of these known ER fluids is limited to about -10°C to about $+60^{\circ}\text{C}$, which prevents their widespread adoption in many industries eg the automotive industry, where ER fluids could otherwise be useful.

Additionally, it would also be desirable to improve the strength of the known ER fluids, thereby to permit smaller devices, requiring less power to drive them, to be built. The provision of stronger ER fluids would also allow devices to be operated at lower voltages, which would have advantages in power supply design, and generally would open up other application areas for the use of ER fluids that are currently beyond the capabilities of existing ER fluids.

In the light of the deficiencies of the known ER fluids a research programme has been undertaken to find a replacement base liquid for the chlorinated paraffins which are currently used in the polymer-based ER fluids.

In GB-A-1570234 it is suggested that Fluorolube FS-5, a polymer of trifluorovinyl chloride manufactured by the Hooker Chemical Company of New York, and Fomblin, a perfluoro polyether fraction marketed by Montedison, are suitable for use as the base liquid. However, our work indicates that fluorinated hydrocarbons are, in general, less satisfactory than chlorinated paraffins. Thus, for example, we have investigated LMAA-containing ER fluids using Fluorolube FS-5 and fluorobenzene as the base phase, and we have found in both cases that the strength of the resulting ER fluids is poor as compared with ER fluids utilizing the standard chlorinated paraffin, viz Cereclor 50LV available from ICI plc.

ER fluids based on silica gel as the dispersed phase and silicon oil as the base liquid phase are described in US-A-3047507 and US-A-4645614. Our own tests using conventional silicone oils as the base liquid have, however, proved disappointing, resulting at best in ER fluids which are weaker than the standard chlorinated paraffin systems.

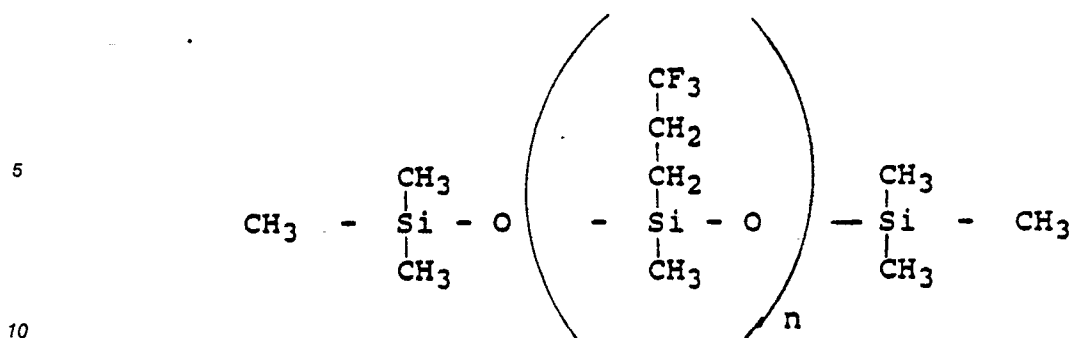
Recent attempts by other workers to find improved base liquids for ER fluids are described in GB-A-2100740 and GB-A-2153372.

We have now unexpectedly found in accordance with the present invention that certain fluorinated silicone oils can provide ER fluids of improved properties. More particularly, the base liquids which we use in this invention are polyfluoroalkylmethyl siloxanes, and we have found that such liquids can be employed in conjunction with a wide variety of substances as the solid phase to provide novel ER fluids of desirable properties, and, in the preferred embodiments, with properties superior to those of ER fluids currently available in commerce especially as regards strength and stability.

Thus, the present invention broadly provides an ER fluid of the type comprising a solid phase dispersed in a base phase liquid, wherein the base liquid comprises a perfluoroalkylmethyl siloxane.

As already indicated, a wide variety of solid materials may be used to form the dispersed phase in the ER fluids of this invention, amongst which can be mentioned acid group-containing polymers, silica gel, starch and electronic conductors, by way of example.

We currently prefer to employ as the base liquid polymethyl 3,3,3-trifluoropropylsiloxane or polymethyl 1,1,2,2-tetrahydropentafluorooctylsiloxane, both of which are commercially available. A particularly preferred embodiment uses polymethyl 3,3,3-trifluoropropylsiloxane of the general formula:



wherein n is selected to provide a liquid having an average molecular weight of about 500 to about 15,000.

15 Such liquids are available from Dow Corning Silicones under the designation FS 1265.

Polymethyl 1,1,2,2-tetrahydroperfluorooctylsiloxane is available from Petrarch Systems, Inc., U.S.A.

Other polyfluoroalkylmethyl siloxanes can be prepared by known methods.

The base fluid may suitably have a viscosity up to about 10,000 cs at 25°C, but for the majority of applications the viscosity should lie in the range about 30-1000 cs at 25°C, preferably about 30-500 cs as 25°C, more preferably about 80-300 cs at 25°C, and most preferably about 80-100 cs at 25°C. The polymethyl 3,3,3-trifluoropropylsiloxane available from Dow Corning Silicones under the designation FS 1265 is supplied with a viscosity of either 300 cs at 25°C or 10,000 cs at 25°C. A desired viscosity within the ranges indicated above may be obtained by distillation and/or blending of these commercially available products. Thus, the most preferred embodiment of this invention currently uses a distillation fraction of 25 FS1265/300 cs which has a viscosity of about 100 cs at 25°C.

One preferred class of materials to form the dispersed phase of the ER fluids of this invention are the acid group-containing polymers which are taught in GB-A-1570234, hereby incorporated by reference. We prefer to employ acid-group containing polymers in which the acid groups are free or at least partially neutralized, particularly by metal cations selected from Groups I, II and III of the Periodic Table, such as 30 lithium, sodium, potassium, copper, magnesium, aluminium and chromium. As regards the polymeric backbone, a particularly preferred class of polymer is an addition polymer containing at least one monomer which has at least one acid group and/or at least one group convertible to an acid group after polymerization. Exemplary of such monomers are acrylic acid, methacrylic acid, methyl acrylate and methyl methacrylate.

35 The currently most preferred acid group-containing polymers are the metal salts of polymethacrylic acid, and especially the lithium salt, ie LMAA, since these have been found to give the strongest ER fluids with the lowest current consumption.

The molecular weight of the solid polymer is not critical, since variations in molecular weight do not appear to have a significant effect on the rheological or other properties of the ER fluid. However, we 40 typically use LMAA with a molecular weight in the range 20,000 -30,000.

In order for an ER effect to be exhibited using acid group-containing polymers as the dispersed phase, it is necessary for a small amount of water to be present in the ER fluid, as is well known to those skilled in this art.

Whilst the commercially available ER fluids based on LMAA utilize LMAA with a pH of about 9, we 45 prefer to employ LMAA with a somewhat lower pH, preferably of the order of pH 6.25 - 7.00. Thus, we have found that whilst a lower pH does not significantly alter the ER effect, it does achieve a considerable reduction in current consumption, up to a factor of three times or even more. The preferred water content of the ER fluid depends on the pH of the system, since it is desirable that there should be a rough equivalence between the lithium ion concentration and the number of water molecules. At pH 7.0, for 50 example, the preferred water content of the ER fluid is approximately 12% as measured using an IR dryer (the water content measured is that driven off by the dryer, not the total water present). At pH 9.0 on the other hand, the preferred water content is about 15.5%, as measured by the same technique.

The successful development of electrorheological properties with other substances conventionally used to form the dispersed phase, for example starch and silica gel, also requires the presence in the ER fluid of 55 a minimum amount of water. However, a new class of solid phase materials which function under anhydrous conditions has recently been disclosed in GB-A-2170510, which is hereby incorporated by reference. These new solid phase materials are electronic conductors, particularly organic semiconductors, and such may be used in conjunction with polyfluoroalkylmethyl siloxane base liquids in accordance with the present

invention to provide ER fluids of particularly advantageous properties.

As in the prior art ER fluids, the particle size of the solid phase preferably should lie within the range from 1-50 microns, and more preferably be from 2-25 microns. Typically we have successfully used LMAA with a mean particle size of about 10 microns.

In general, the amount of the solid used to form the dispersed phase will be within the range employed in known ER fluids, and typically will be from 20% to 40% by volume of the fluid. However, the ER effect is observable at lower solid phase loadings, even down 5% v/v, and similarly a loading of 40% v/v does not represent the maximum which can be used.

The ER fluids of this invention may be prepared by conventional techniques. We used the following method to prepare an ER fluid containing LMAA dispersed in polymethyl 3,3,3-trifluoropropylsiloxane. Polymethacrylic acid is neutralized with lithium hydroxide to a desired pH, following which the aqueous solution of LMAA is spray dried, and the resulting dried polymer is ground in a small mill. At this time, the water content of the polymer is measured by driving off the water using an IR dryer, and adjusted if required. Adjustment is effected using a fluidized bed dryer to reduce the water content, or by allowing it to gain water under vacuum in a vacuum chamber if it is necessary to hydrate the polymer. The required quantity of LMAA, of the desired water content, is now dispersed in the polymethyl 3,3,3-trifluoropropylsiloxane base liquid and then milled in a bead mill for a time sufficient to reduce the particles to the required size range.

If desired, a dispersant such as a hydrogenated castor oil may be incorporated, but it is an advantage of the present ER fluids that they are in general quite physically stable and do not require the inclusion of a dispersant to maintain the solid phase sufficiently dispersed.

In addition to their physical stability, the present ER fluids are also stable chemically with respect to temperature, and in particular do not break down at elevated temperatures to corrosive by-products. This permits the ER fluids to be used over a wider temperature range than was hitherto possible with the standard LMAA-chlorinated paraffin systems.

Other advantages of the present ER fluids in preferred instance are that they are stronger than the conventional LMAA-chlorinated paraffin systems, and that their low temperature viscosity is lower, and the viscosity varies less with temperature, than the conventional systems.

The invention is illustrated by the Example which follows:

Example

A number of ER fluids were prepared in the following manner.

Polymethacrylic acid, with a molecular weight of about 25,000, was neutralized to pH of about 9 by the addition of lithium hydroxide. The resulting solution of the lithium salt of the polymer was spray dried to remove the major portion of the water, and then carefully dried in a fluidized bed drier to the final water content. The polymer was then mixed with the selected liquid forming the continuous phase and milled in a bead mill for approximately ten minutes. The polymer loading was in each case 35% by volume.

ER fluids were prepared in this manner using the following liquids as the continuous phase:

Liquid Designation	Description of Liquid
S300	polymethyl 3,3,3-trifluoropropylsiloxane available from Dow Corning Silicones under the designation FS 1265 - viscosity 300 cs at 25° C
S100	distillation product of S300 with a viscosity of 100 cs at 25° C
F300	clear, colourless low volatility polydimethylsiloxane available from Dow Corning Silicones - viscosity 300 cs at 25° C
F100	as F300, but with a viscosity of 100 cs at 25° C
50LV	chlorinated paraffin available from ICI plc under the trade mark Cereclor 50LV

The mean particle size of the LMAA in the ER fluids was about 12 microns, and the water content varied from 15.5 - 16.1%.

The resulting ER fluids were then tested in the electro-rheological viscometer which is shown schematically in Fig. 10 of the accompanying drawings. As illustrated, this viscometer comprised a bob

rotating in a static cup which contained the test ER fluid which filled the gap (about 0.5 mm) between the cup and the rotor. A voltage was applied to the cup and the rotor turned. Voltage and speed were varied to give steps of field and shear rate. Temperature was maintained at 50° C by a circulator (not shown). Shear stress was measured by a torque transducer at the bottom of the cup. The results obtained are shown graphically in Figures 1-9 of the accompanying drawings, as follows:

Figs. 1, 4 and 7 are so-called "flow curves" showing how the shear stress varied with the shear rate at zero applied voltage and at 2.32 Kv/mm, respectively, for each of the ER fluids of this invention (F300 and F100) and the comparative ER fluids (S300, S100 and 50LV);

Figs. 2, 5 and 8 are plots for the test ER fluids of excess shear stress against field strength -the excess shear stress is the shear stress at zero volts subtracted from the total shear stress, and serves to provide a better assessment of the influence of the electrical field; and

Figs. 3, 6 and 9 are plots for the test ER fluids of current density against field strength.

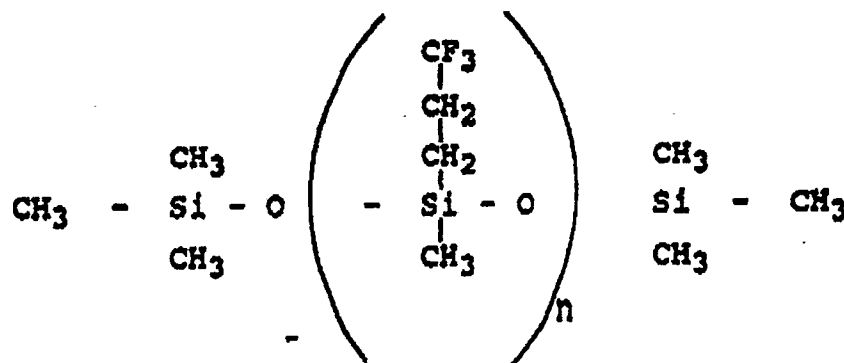
The measurements were made at 50° C and at a shear rate of 125 sec⁻¹.

Claims

1. An electro-rheological fluid of the type comprising a solid phase dispersed in a base liquid, wherein the base liquid comprises a polyfluoroalkylmethyl siloxane.

2. An electro-rheological fluid according to Claim 1, wherein said base liquid contains at least one compound selected from polymethyl 3,3,3-trifluoropropylsiloxane and polymethyl 1,1,2,2-tetrahydroperfluorooctylsiloxane.

3. An electro-rheological fluid according to Claim 2, wherein said polymethyl 3,3,3-trifluoropropylsiloxane has the general formula:



wherein n is selected to provide a liquid having an average molecular weight of about 500 to about 15,000.

4. An electro-rheological fluid according to Claim 1, wherein said base liquid has a viscosity up to about 10,000 cs at 25° C.

5. An electro-rheological fluid according to Claim 4, wherein said base fluid has a viscosity of about 30 to about 1,000 cs at 25° C.

6. An electro-rheological fluid of Claim 5, wherein said base fluid has a viscosity of about 30 to about 500 cs at 25° C.

7. An electro-rheological fluid according to Claim 6, wherein said base fluid has a viscosity of about 80 to about 300 cs at 25° C.

8. An electro-rheological fluid according to Claim 7, wherein said base fluid has a viscosity of about 80 to about 100 cs at 25° C.

9. An electro-rheological fluid according to Claim 1, wherein said dispersed phase contains at least one solid compound selected from:

- a) an acid group-containing polymer;
- b) silica gel;
- c) starch; and
- d) an electronic conductor.

10. An electro-rheological fluid according to Claim 9, wherein said compound is an acid group-containing polymer in which said acid groups are free or neutralized.

11. An electro-rheological fluid according to Claim 10, wherein said polymer is an addition polymer.

12. An electro-rheological fluid according to Claim 11, wherein said addition polymer is derived from at least one monomer which contains at least one acid group and/or at least one group which is convertible to an acid group after polymerization of the monomer.

13. An electro-rheological fluid according to Claim 12, wherein said addition polymer is derived from one or more monomers selected from acrylic acid, methacrylic acid, methyl acrylate and methyl methacrylate.

14. An electro-rheological fluid according to Claim 10, wherein at least a proportion of the acid groups of the polymer are neutralized to form salts.

15. An electro-rheological fluid according to Claim 14, wherein the acid groups are neutralized by a metal cation selected from Groups I, II and III of the Periodic Table.

16. An electro-rheological fluid according to Claim 15, wherein the metal cation is selected from lithium, sodium, potassium, copper, magnesium, aluminium and chromium.

17. An electro-rheological fluid according to Claim 16, wherein the polymer is a salt of polymethacrylic acid.

18. An electro-rheological fluid according to Claim 17, wherein the salt is a lithium.

19. An electro-rheological fluid according to Claim 9, wherein said electronic conductor is an organic semiconductor.

20. An electro-rheological fluid according to Claim 1, wherein the solid phase has a particle size of from 1 to 50 microns.

21. An electro-rheological fluid according to Claim 1, wherein the fluid contains from 20% to 40% V/V of the solid phase.

SHEAR STRESS - SHEAR RATE

—△—	F300	E=2.32
—□—	S300	E=2.32
—+—	F300	E=0V
—◇—	S300	E=0V

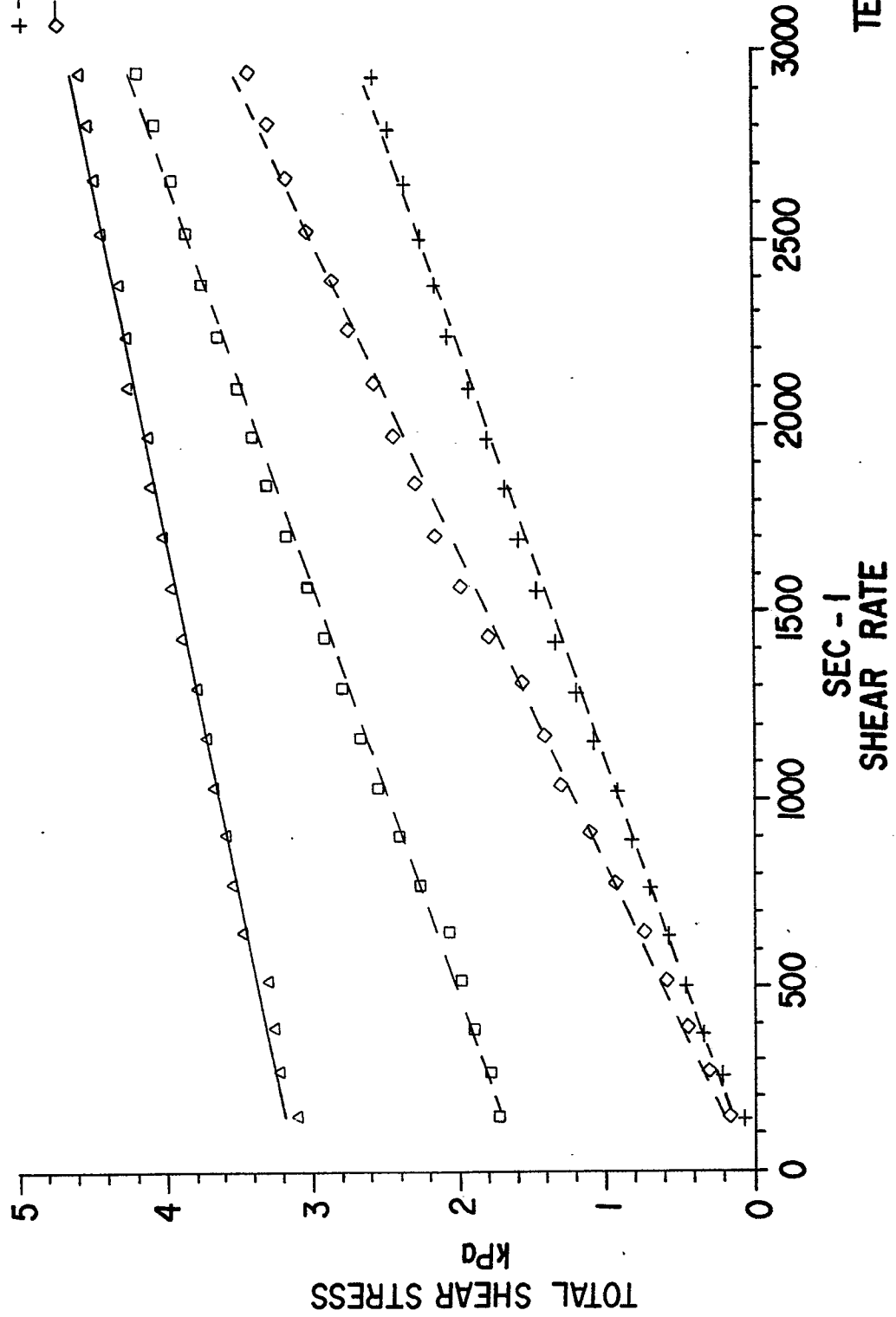
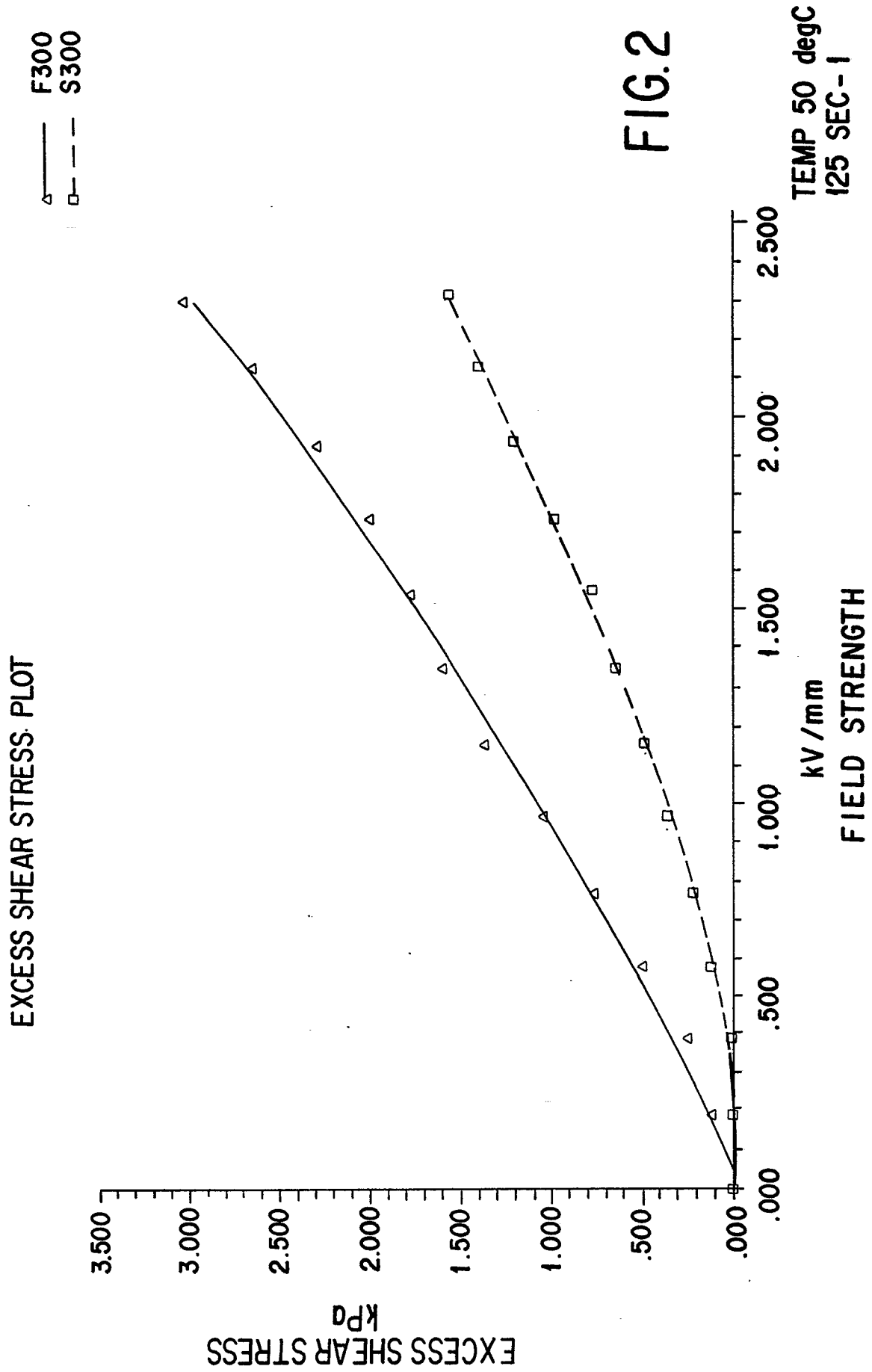


FIG. 1



CURRENT DENSITY PLOT

F300
 S300

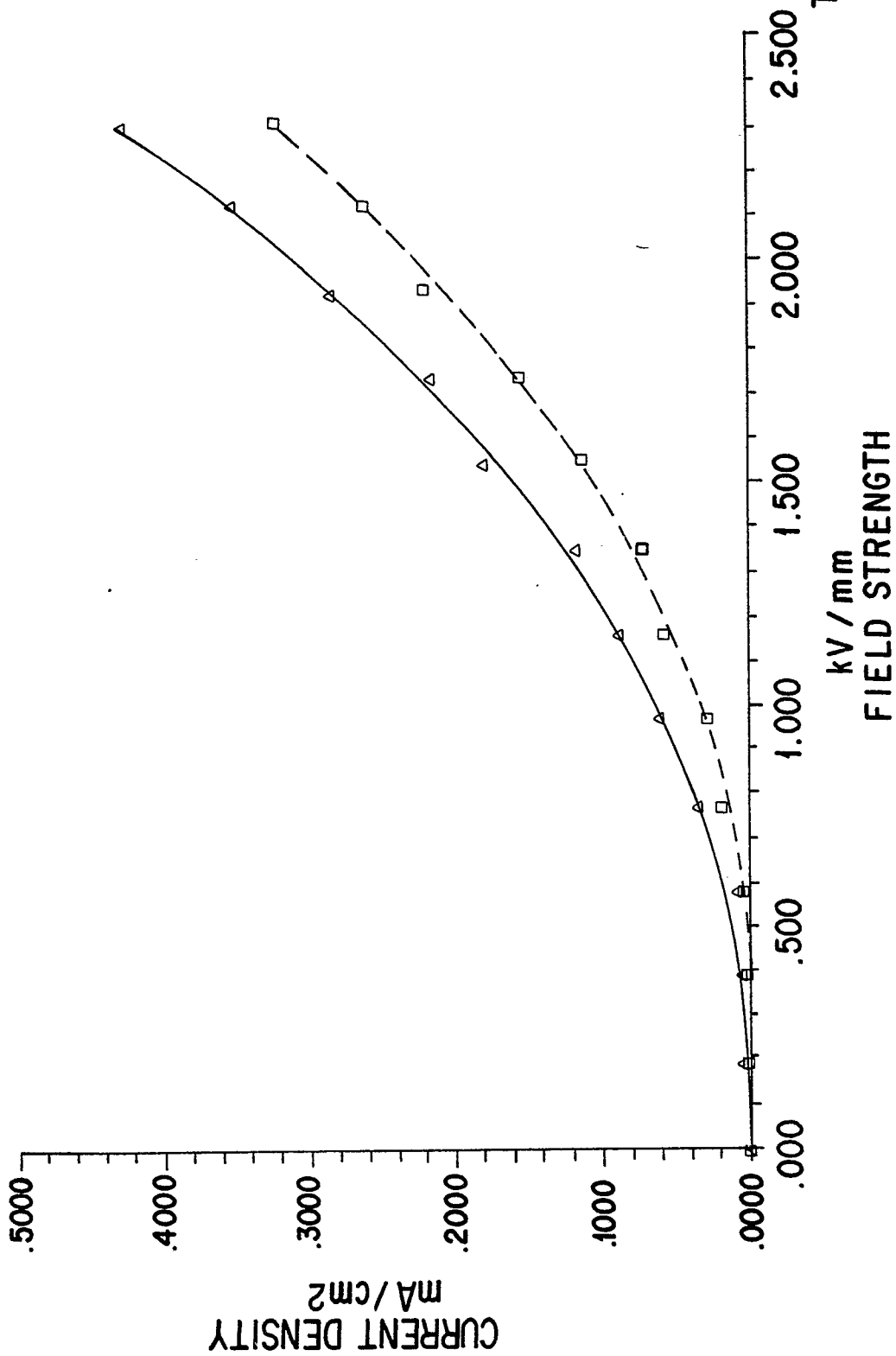


FIG. 3

TEMP 50 degC
 125 SEC-1

SHEAR STRESS - SHEAR RATE

—	F100	E=2.32
- - -	S100	E=2.32
- - -	F100	E=0v
- - -	S100	E=0v

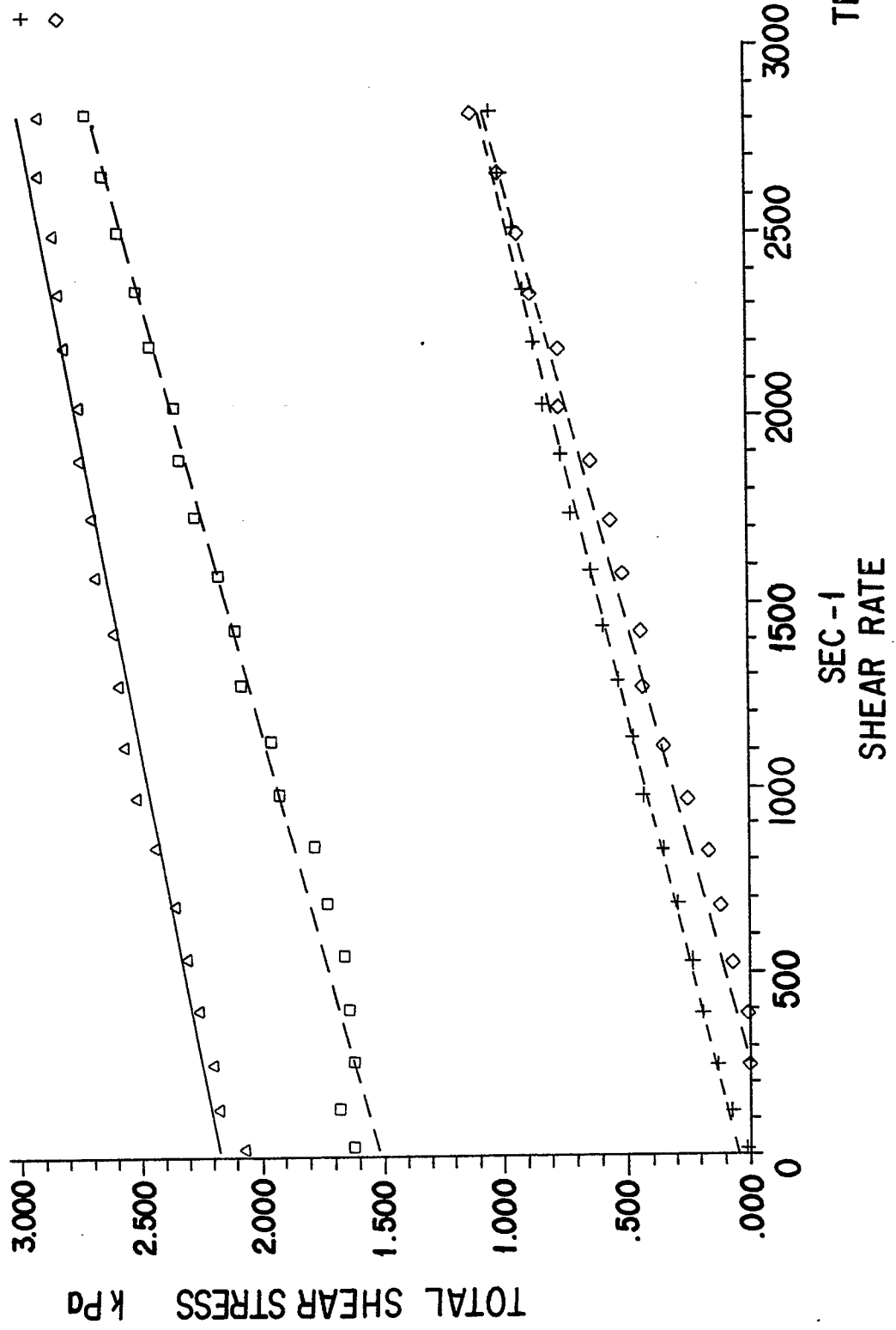
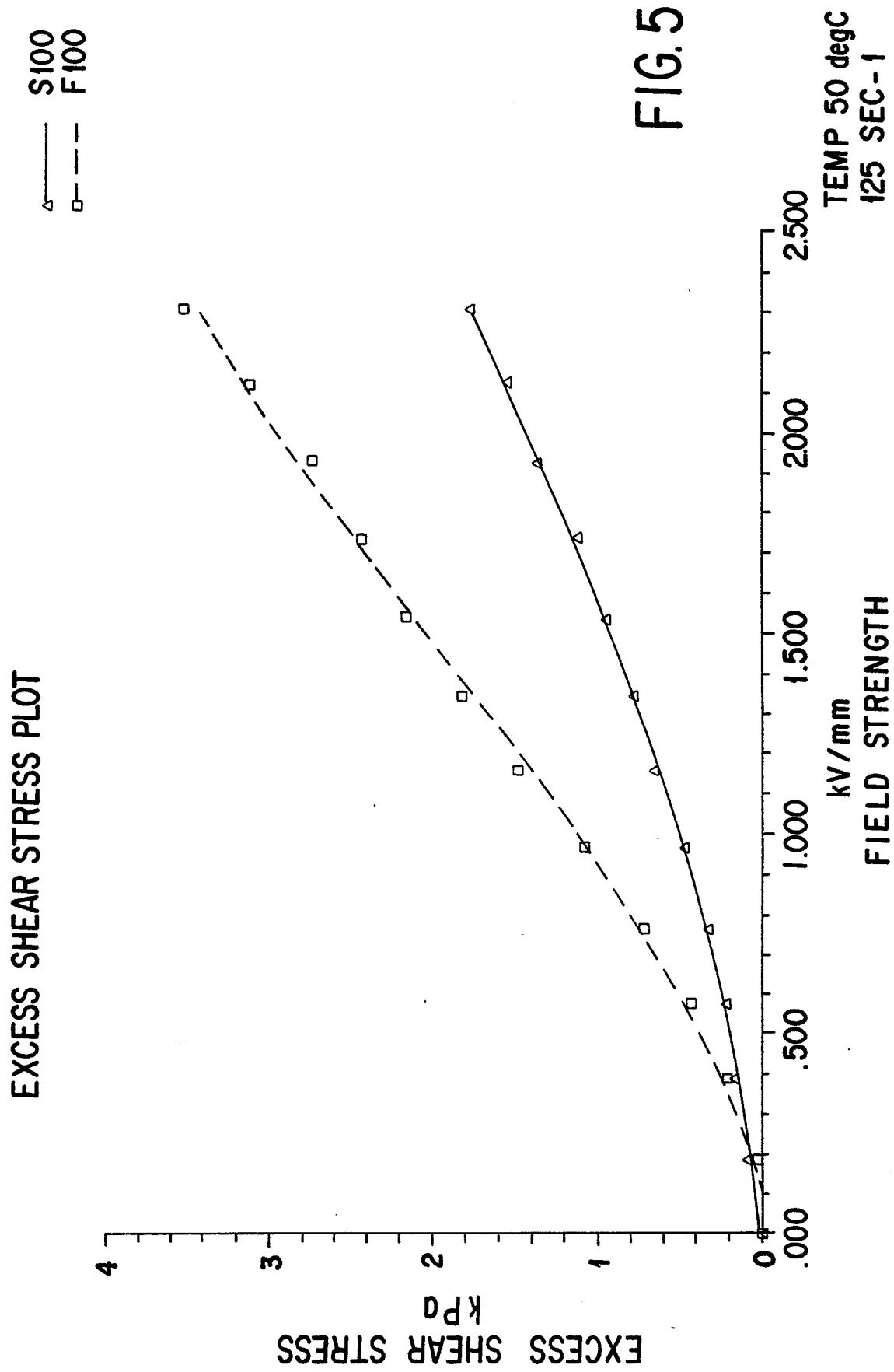


FIG. 4



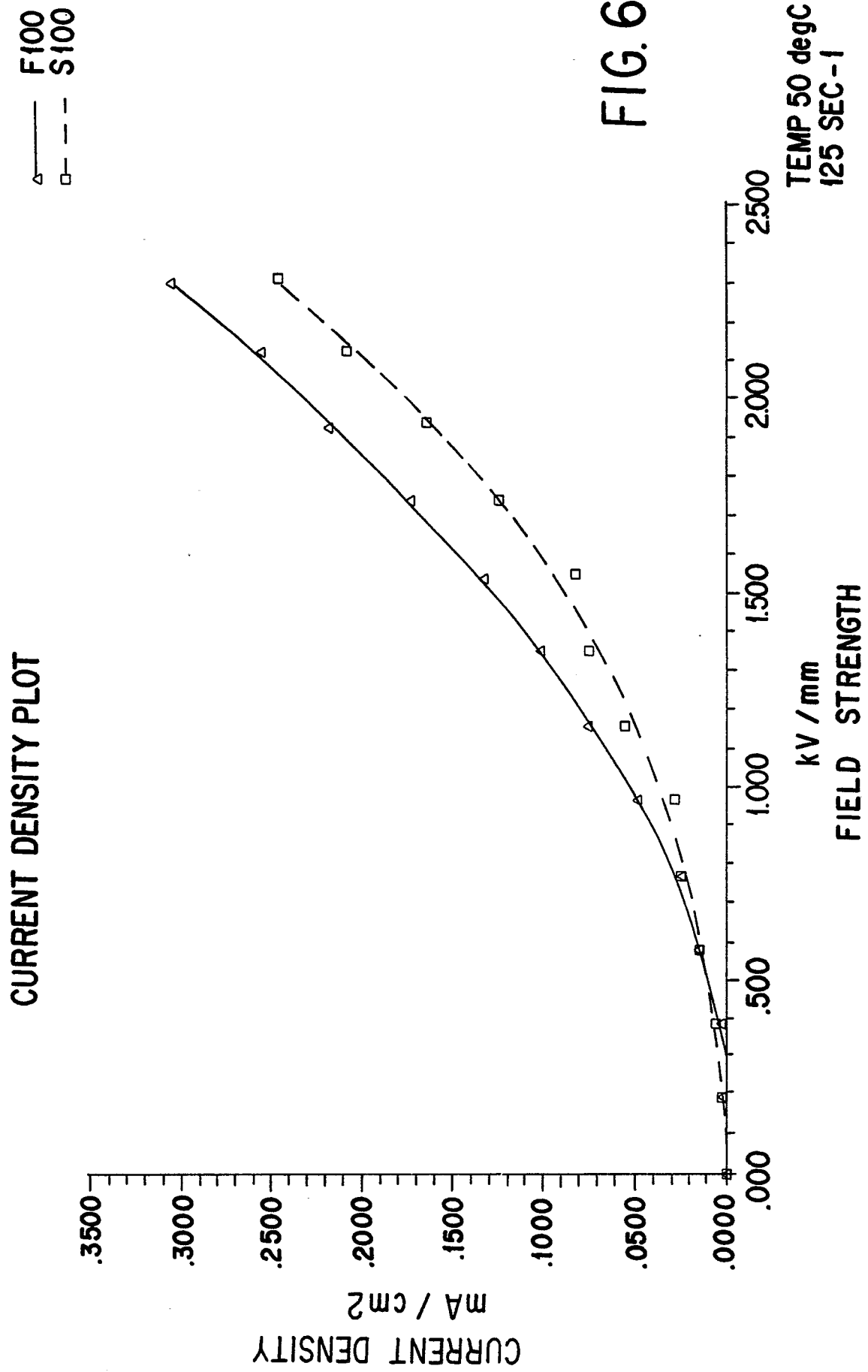
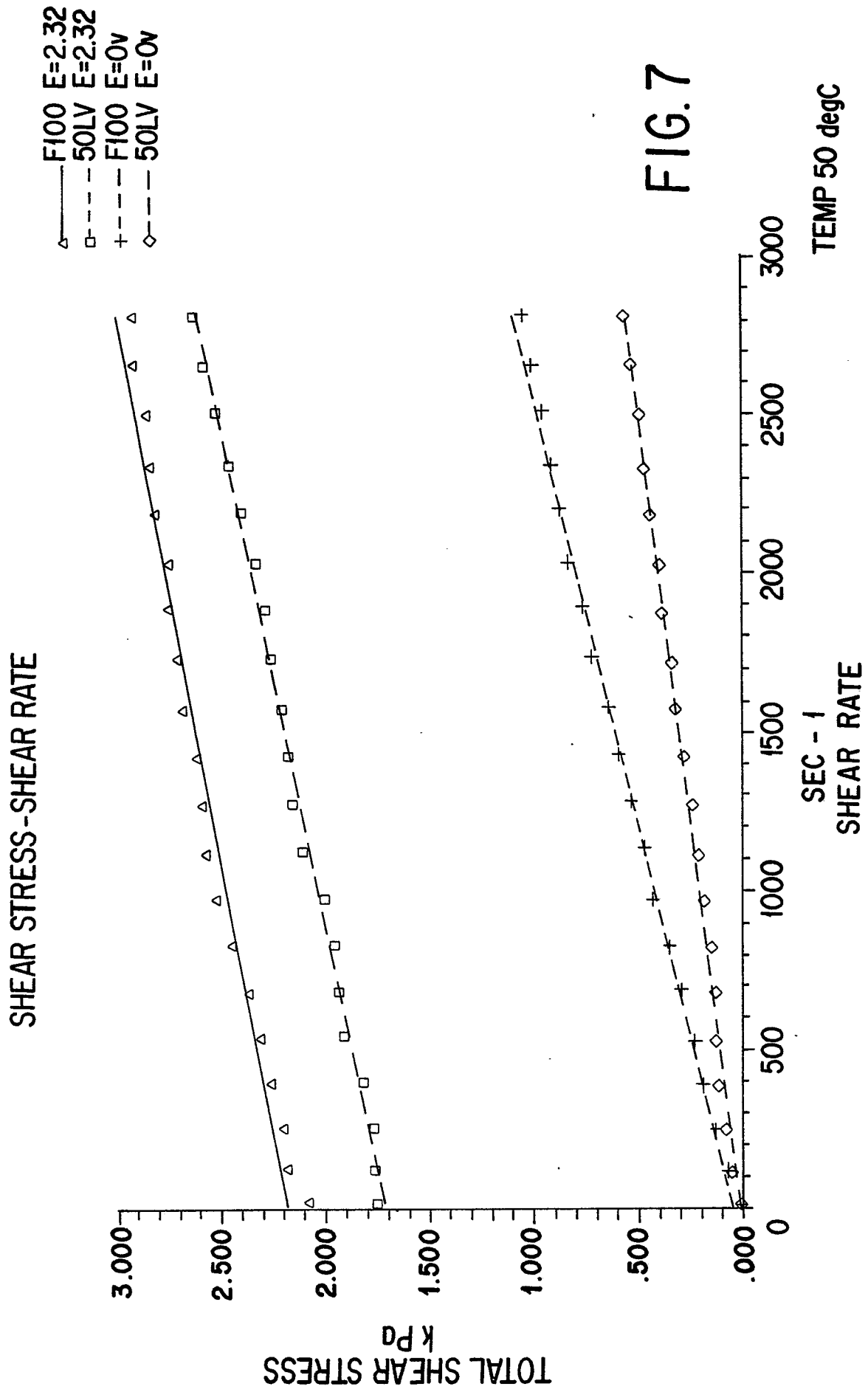
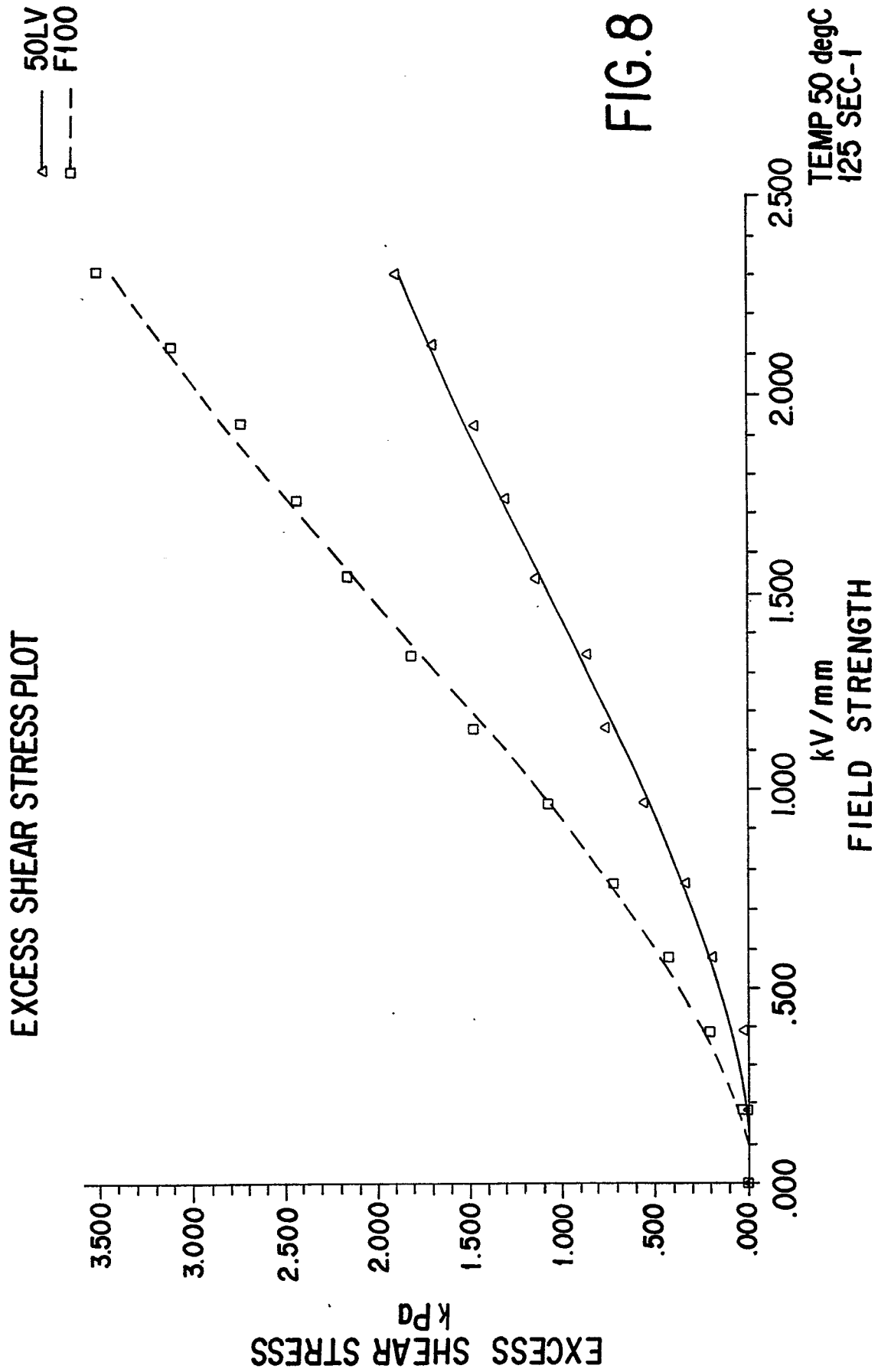


FIG. 6





CURRENT DENSITY PLOT

F100
 50LV

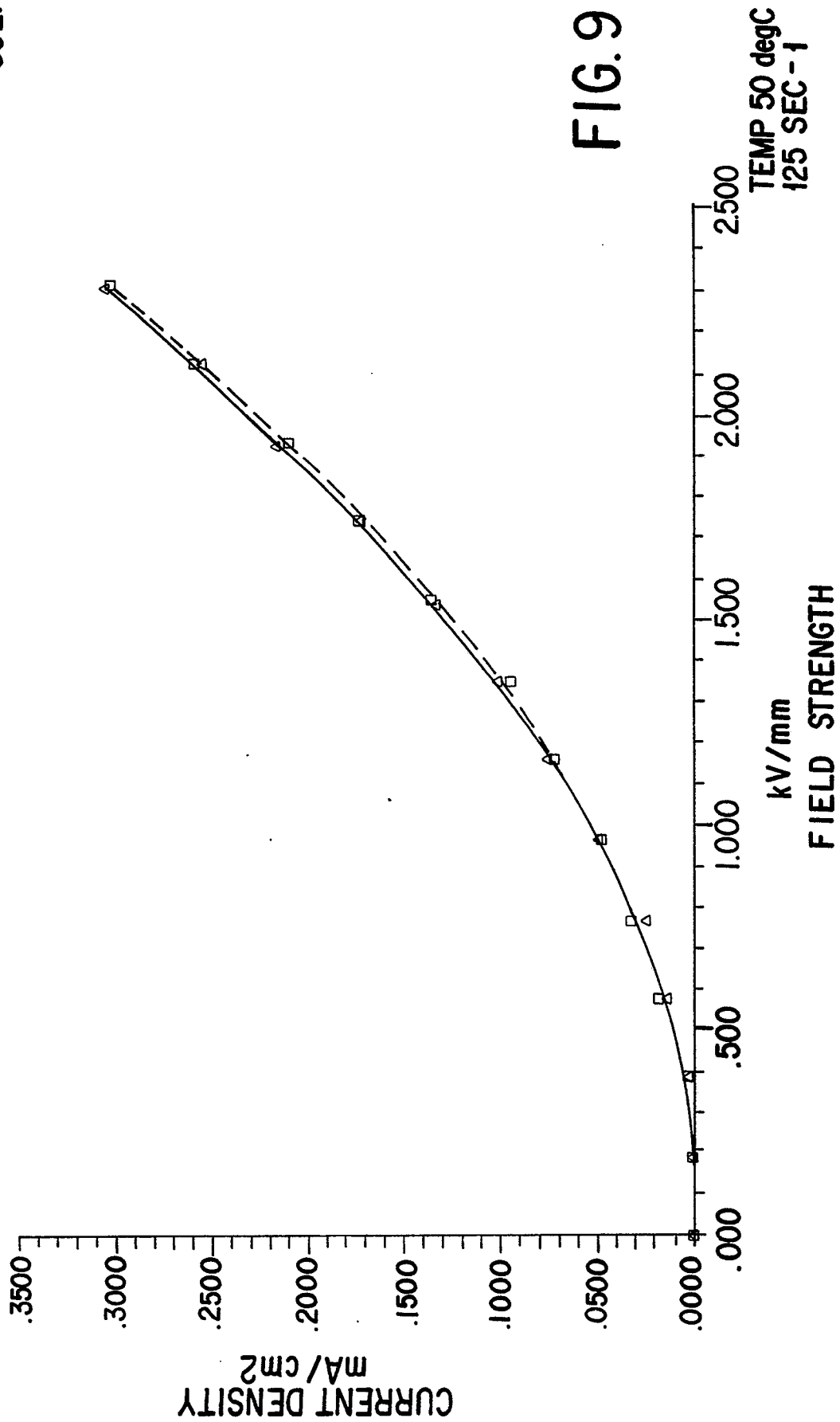


FIG.9

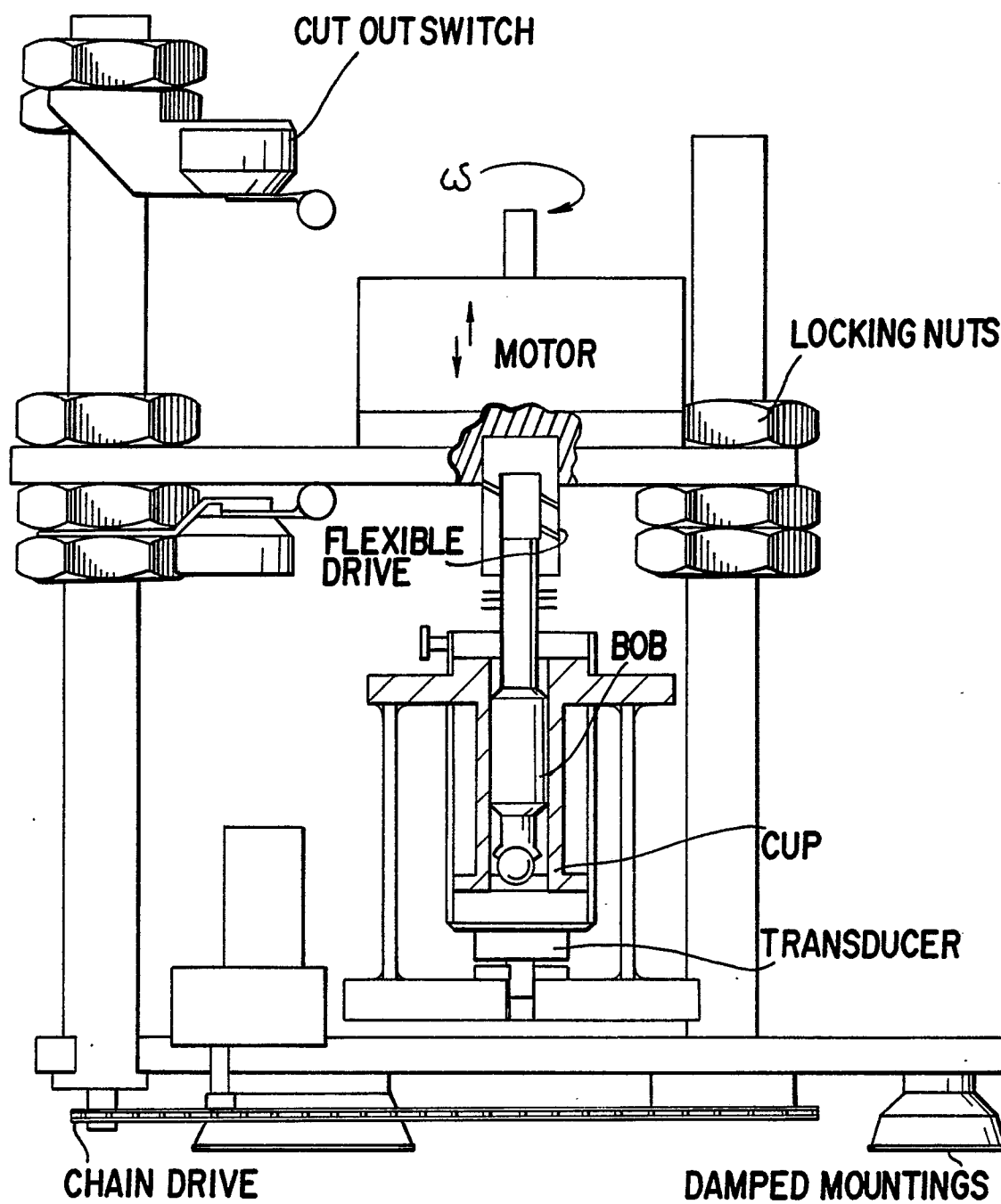


FIG. 10