(12) UK Patent Application (19) GB (11) 2 187 291 (13) A

(43) Application published 3 Sep 1987

(21) Application No 8703394

(22) Date of filing 13 Feb 1987

(30) Priority data
(31) 8600642 (32) 13 Feb 1986 (33) SE

(71) Applicant
Skega AB

(Incorporated in Sweden)

S-934 02 Ersmark, Sweden

(72) Inventor
Sture Persson

(74) Agent and/or Address for Service
Boult, Wade & Tennant,
27 Furnival Street, London EC4A 1PQ

(51) INT CL⁴
G01N 27/22

(52) Domestic classification (Edition I):
G1N 19B2B 19D12AO 19F1B 19H12 19H14
U1S 1529 1626 2159 G1N

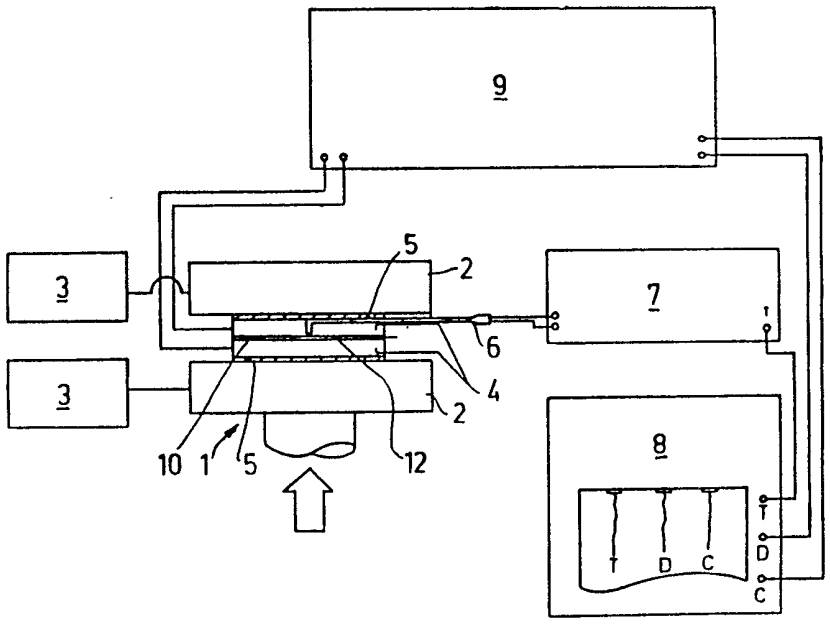
(56) Documents cited
None

(58) Field of search
G1N
Selected US specifications from IPC sub-classes G01N
G01R

(54) Determining basic values of a material specimen

(57) A method and an apparatus for determination of basic values of a material specimen for analysis of its vulcanization characteristic and to enable the study of a vulcanization process during the vulcanization in a rapid and safe manner is provided. The specimen is shaped under pressure and at a temperature preferably in excess of 100°C to a predetermined form and thickness between two electrodes (4) with plane-parallel sides facing each other which, during the shaping process, are brought into an intimate contact with the shaped body to form a capacitor, whereafter the basic values, being the capacitance (C) and loss angle (D) of this capacitor and the temperature of at least one of the electrodes (4), are measured and recorded (8) simultaneously.

FIG.1



GB 2 187 291 A

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

FIG.1

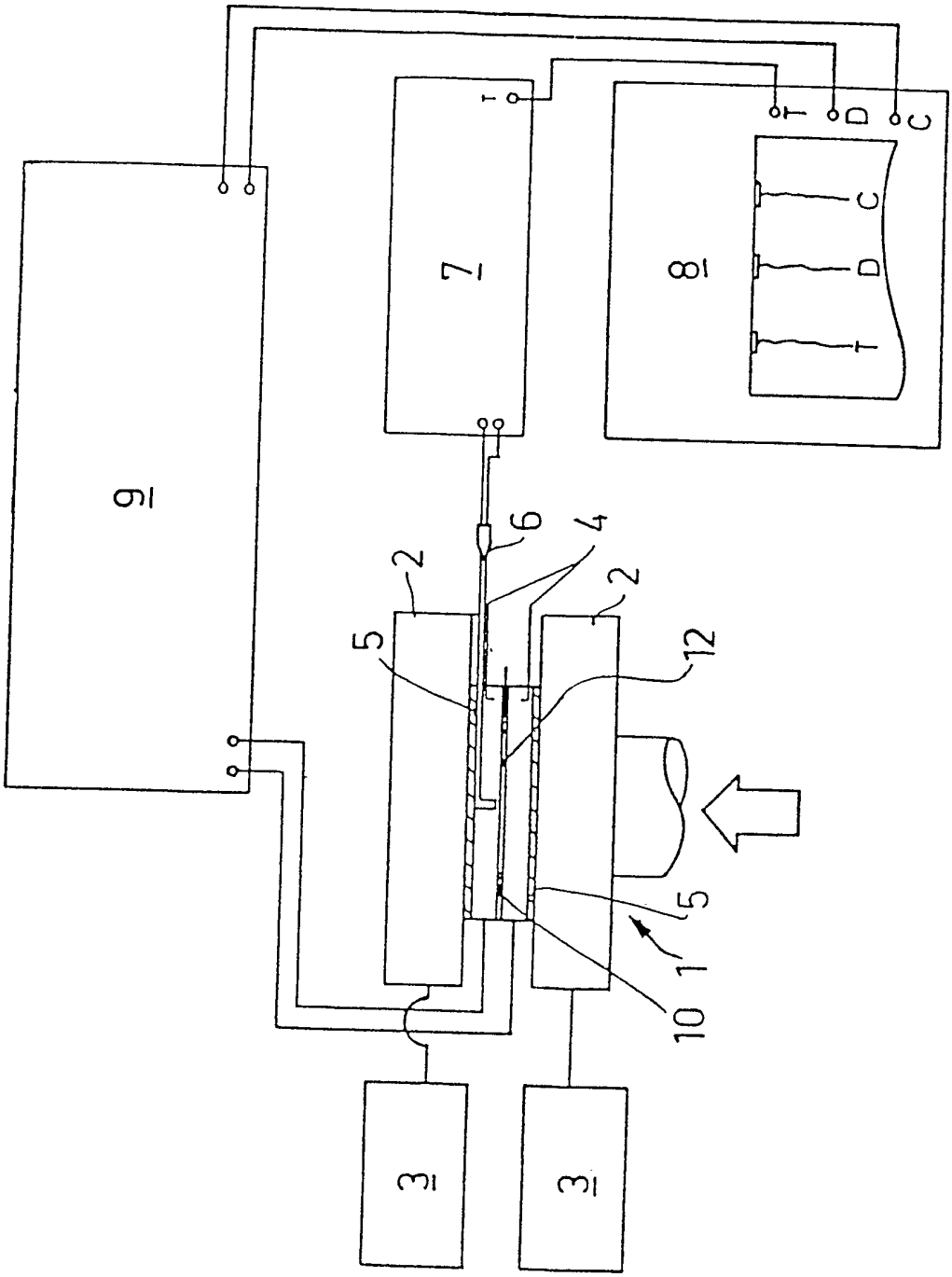


FIG.4

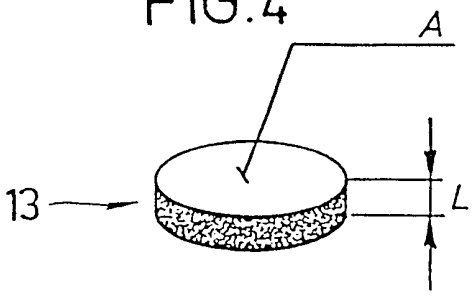


FIG.2

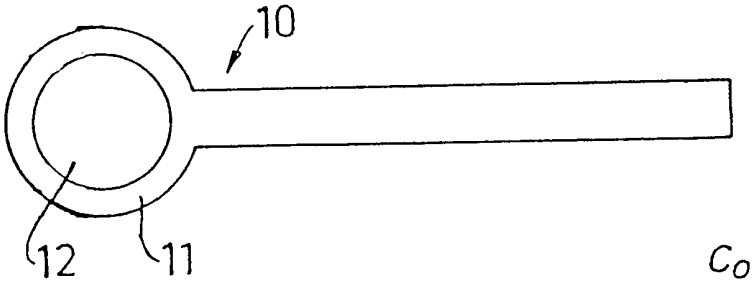


FIG.5

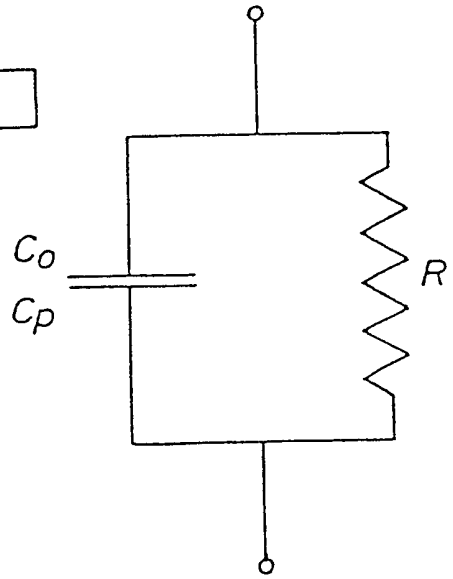


FIG.7

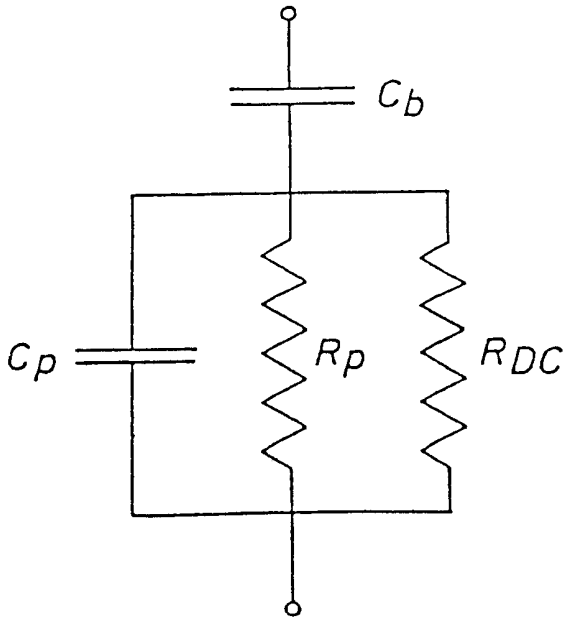


FIG.3

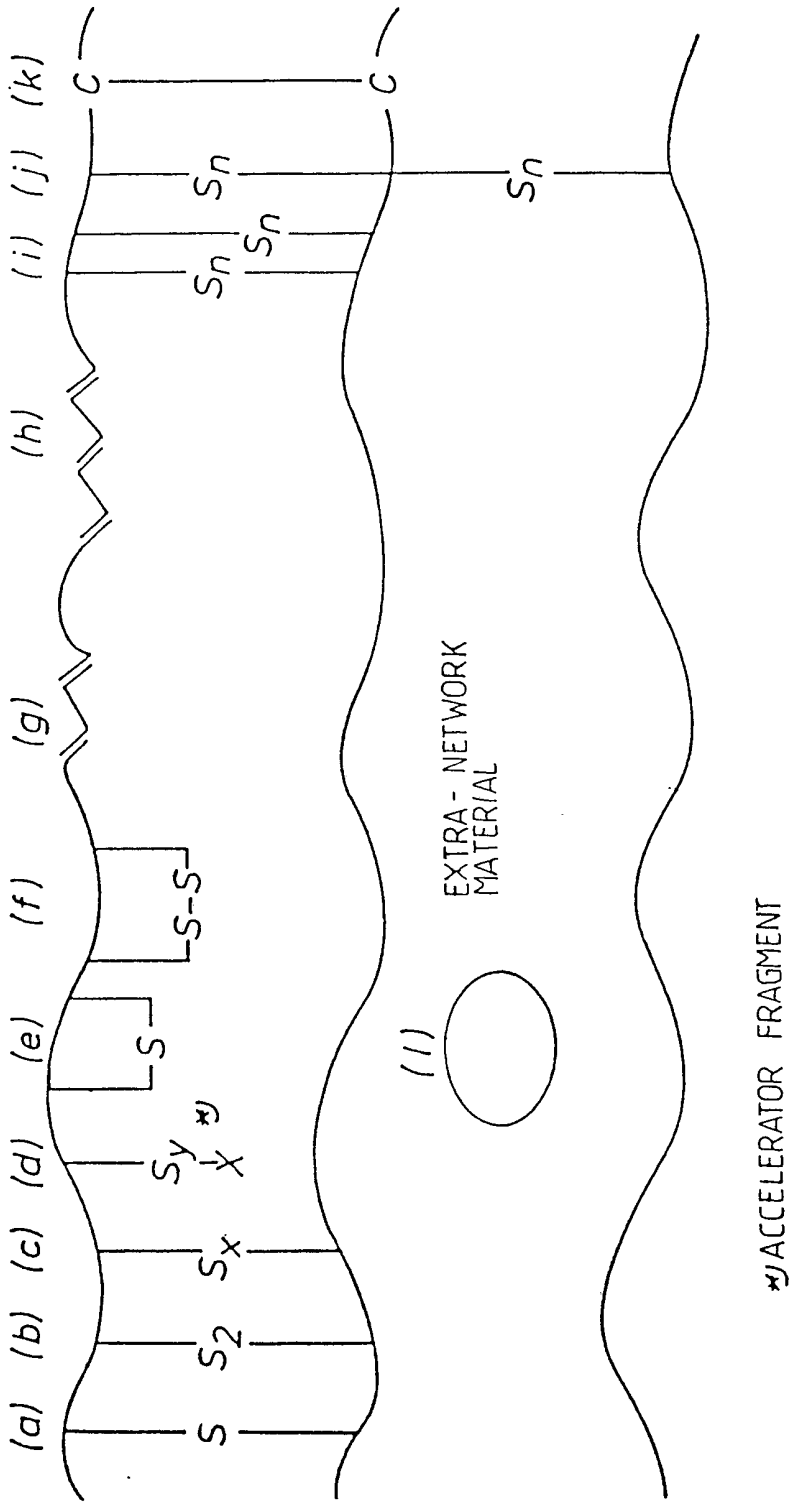

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
S
S2
Sx
Sy
*)
S
S-S
Sn
Sn
Sn
Sn
C
C
EXTRA - NETWORK MATERIAL
*) ACCELERATOR FRAGMENT

FIG.6

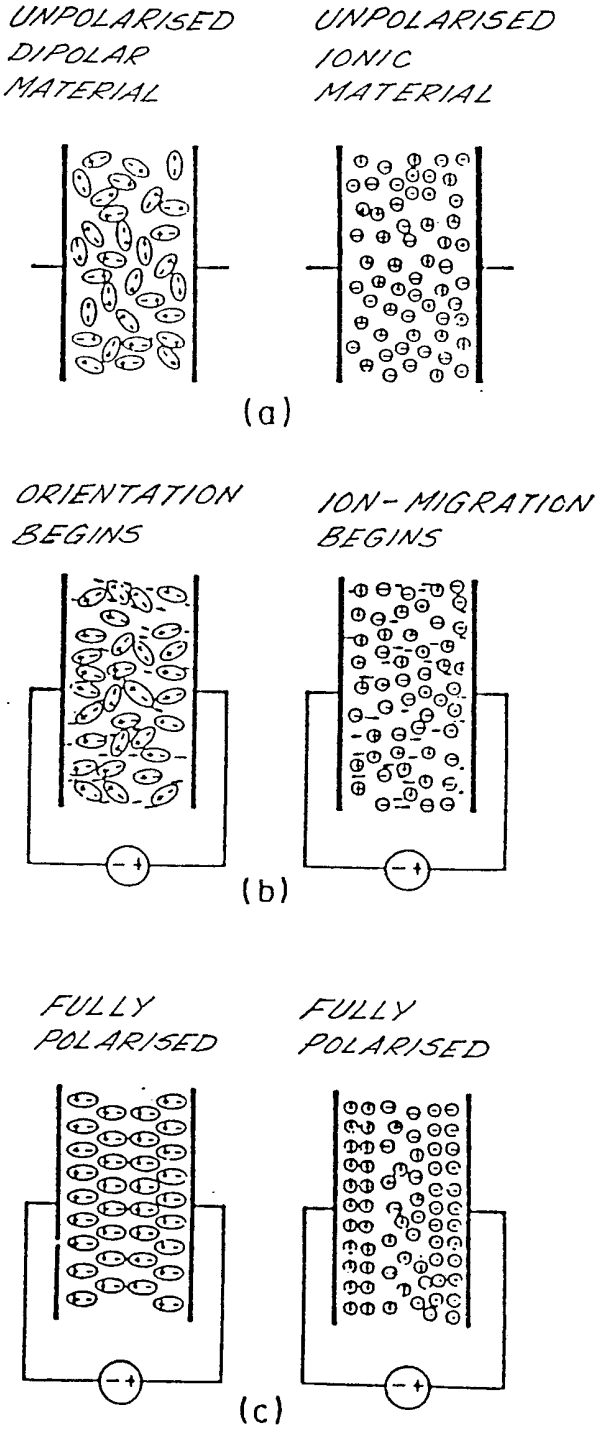

UNPOLARISED DIPOLAR MATERIAL
UNPOLARISED IONIC MATERIAL
(a)
ORIENTATION BEGINS
ION-MIGRATION BEGINS
(b)
FULLY POLARISED
FULLY POLARISED
(c)

FIG.8

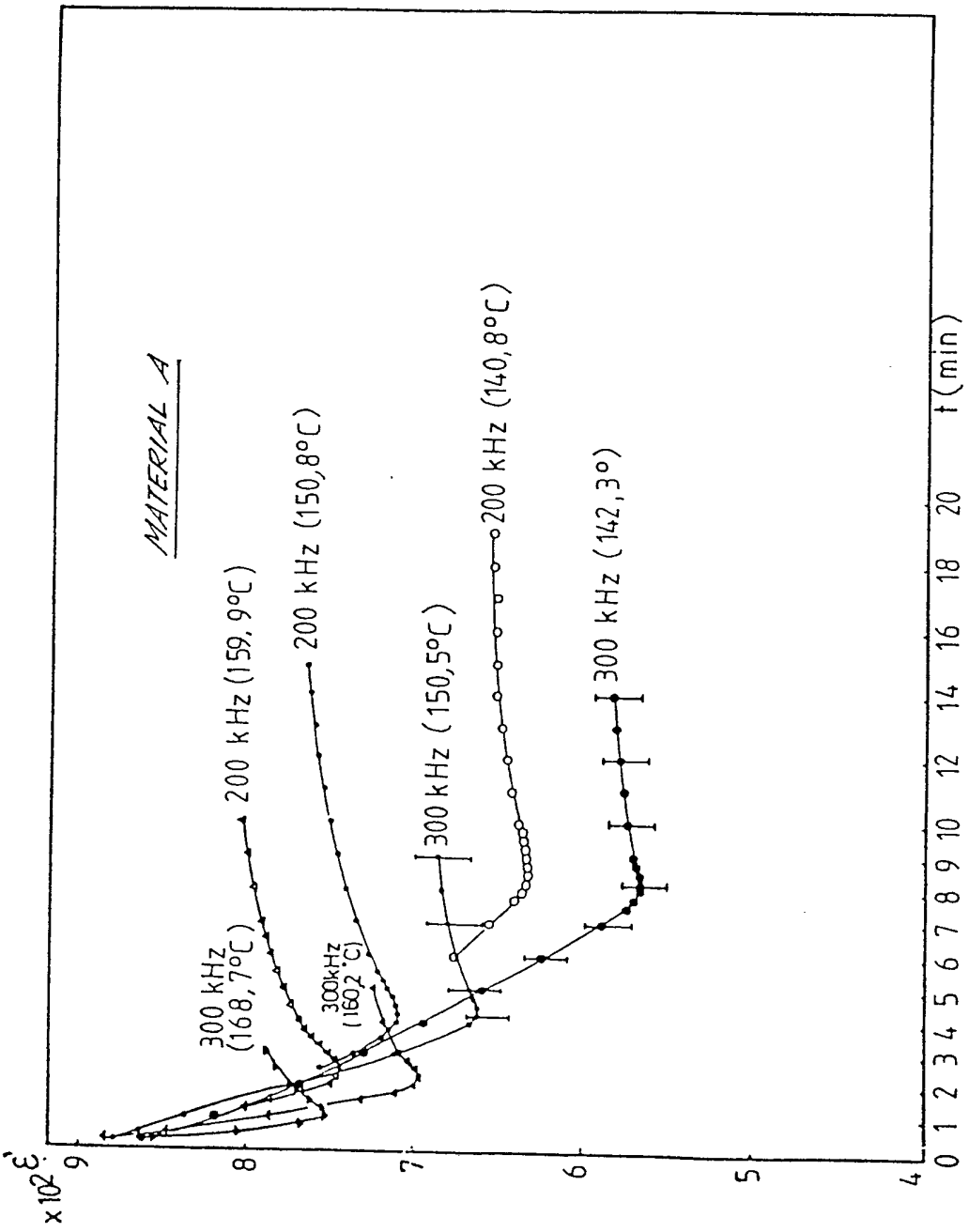

MATERIAL A
200 kHz (159, 9°C)
200 kHz (150,8°C)
300 kHz (168,7°C)
300kHz (160,2°C)
300 kHz (150,5°C)
200 kHz (140,8°C)
300 kHz (142,3°)
x10² ε'
9
8
7
6
5
4
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20
t(min)

FIG.9

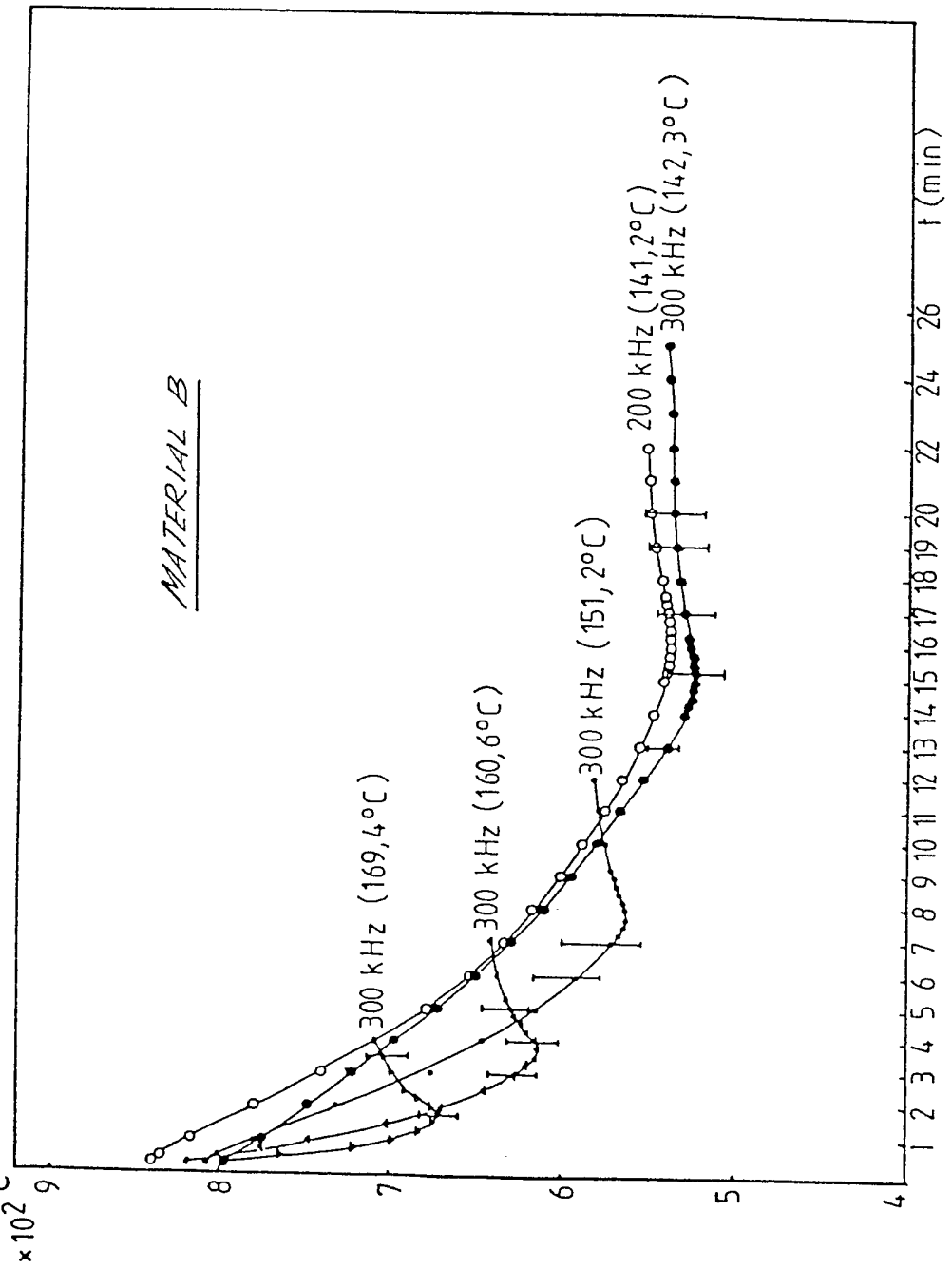

MATERIAL B
300 kHz (169,4°C)
300 kHz (160,6°C)
300 kHz (151,2°C)
200 kHz (141,2°C)
300 kHz (142,3°C)
ε'
x10²
9
8
7
6
5
4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 22 24 26
t (min)

FIG.10

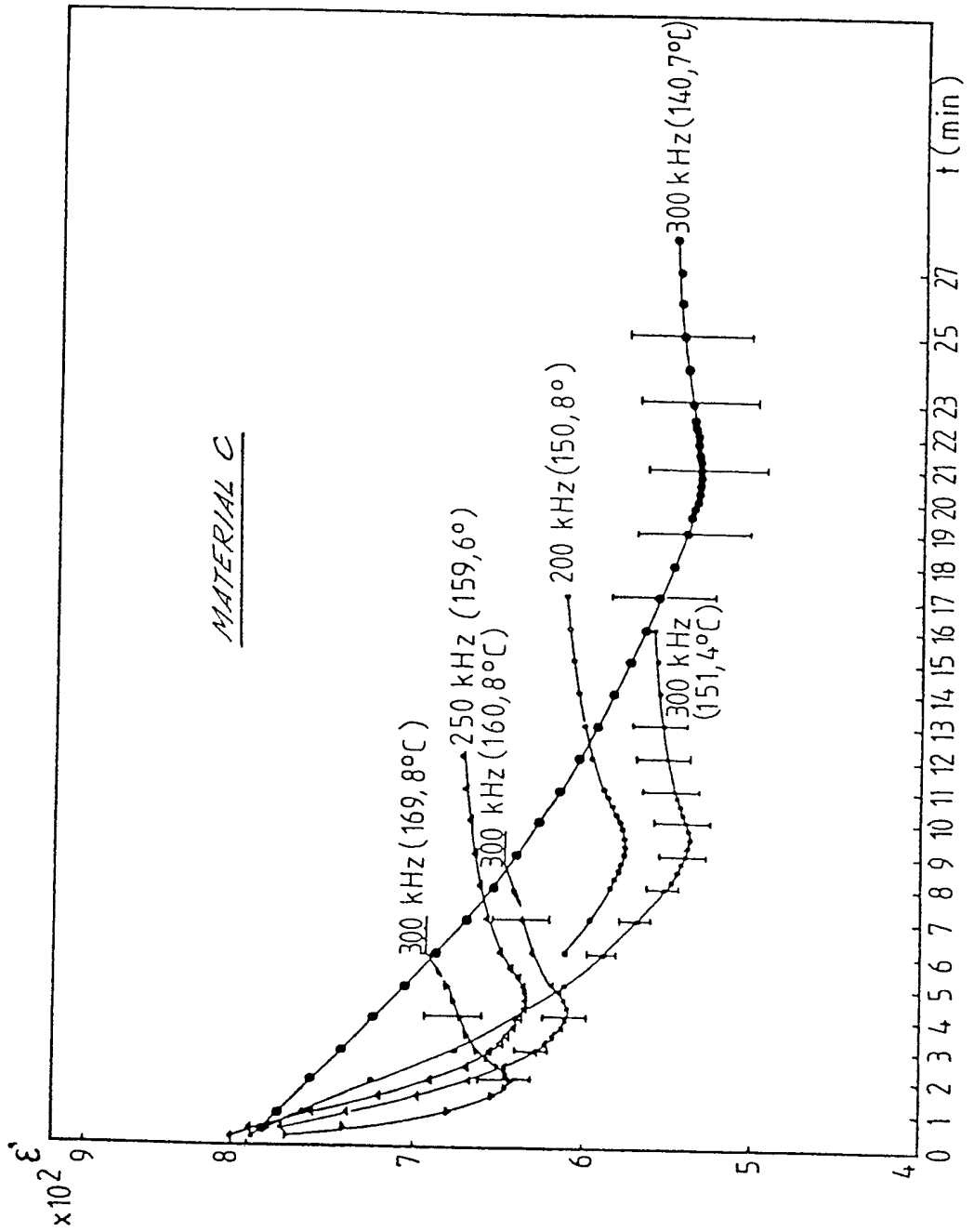

MATERIAL C
300 kHz (169,8°C)
250 kHz (159,6°)
300 kHz (160,8°C)
200 kHz (150,8°)
300 kHz (151,4°C)
300 kHz (140,7°C)
ε'
x10²
t (min)

FIG.11

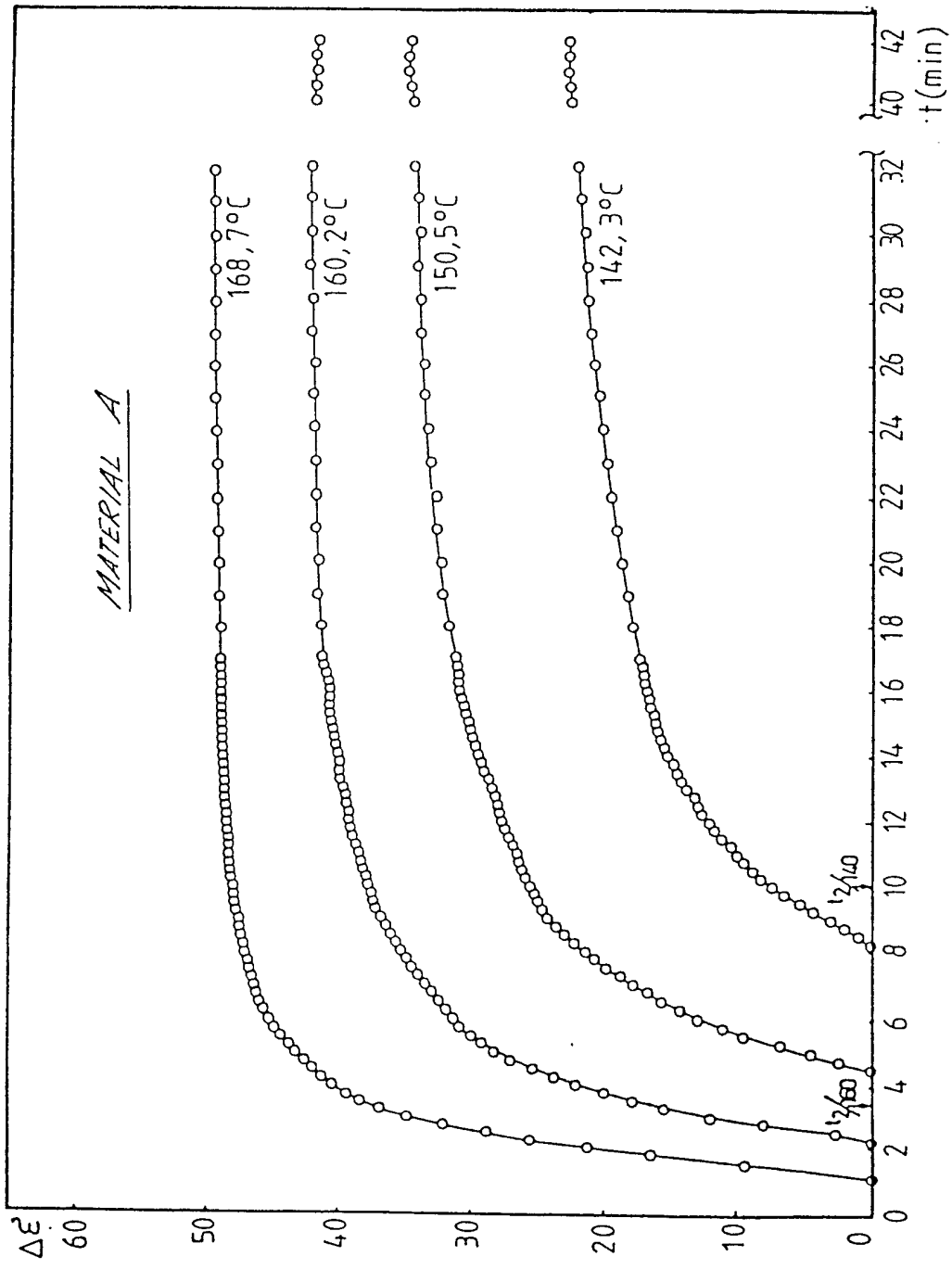

MATERIAL A
168,7°C
160,2°C
150,5°C
142,3°C
Δε'
t(min)
0
10
20
30
40
50
60
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
40
42

FIG.12

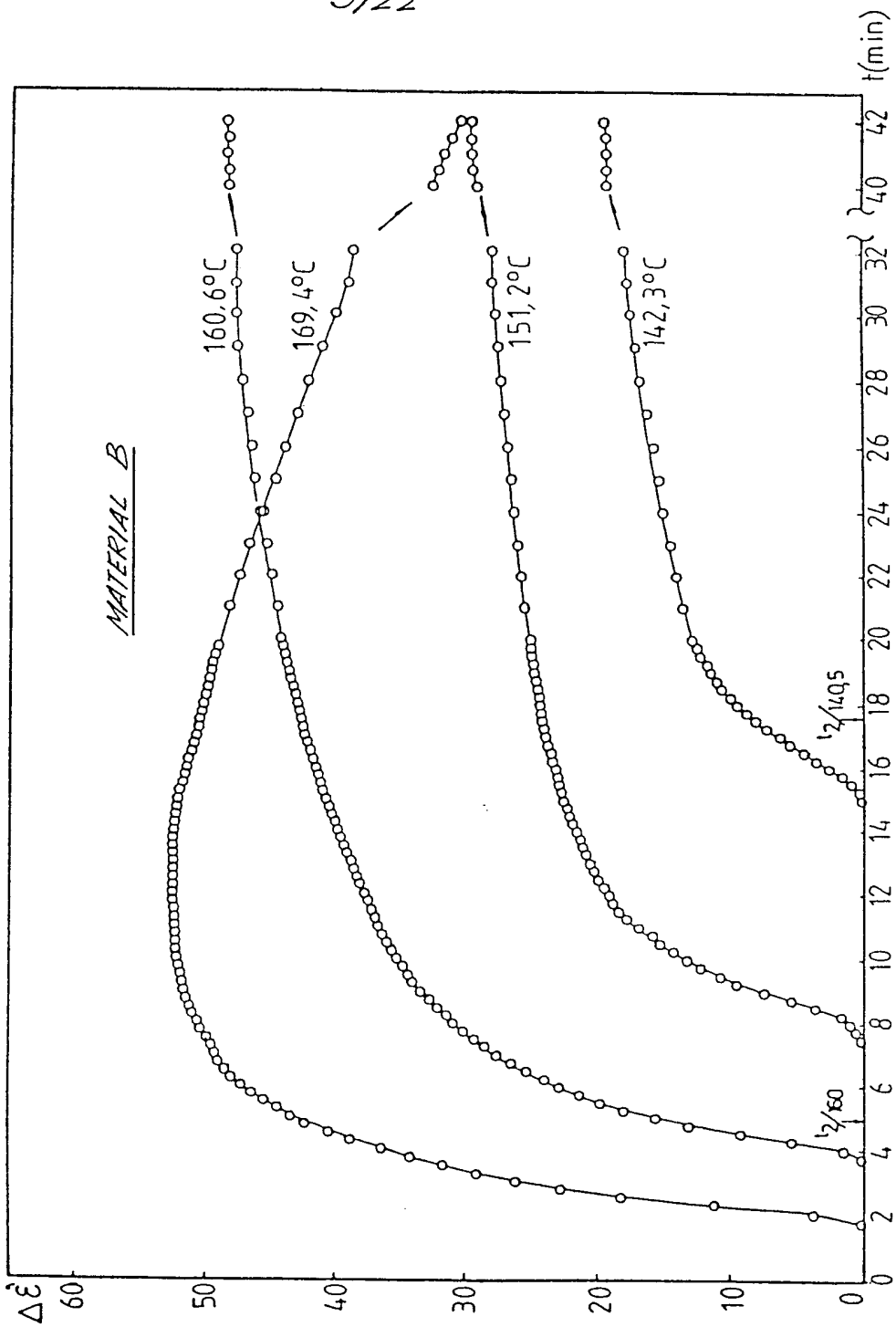

MATERIAL B
160,6°C
169,4°C
151,2°C
142,3°C
t½/160
t½/145
Δε'
t(min)
0
10
20
30
40
50
60
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
40
42

FIG.13

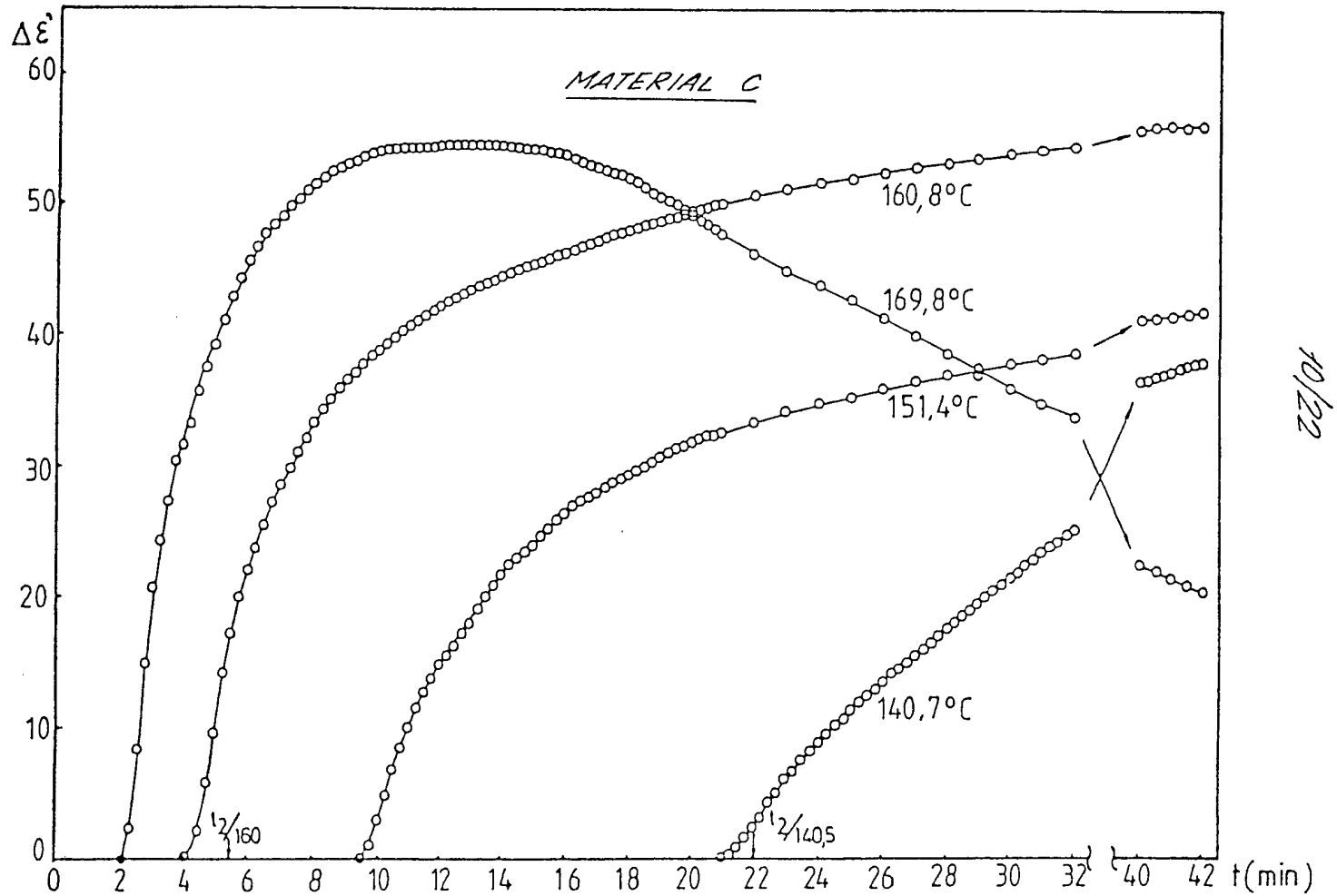

Δε'
MATERIAL C
160,8°C
169,8°C
151,4°C
140,7°C
t2/160
t2/140,5
t(min)
0
10
20
30
40
50
60
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
40
42

FIG.14

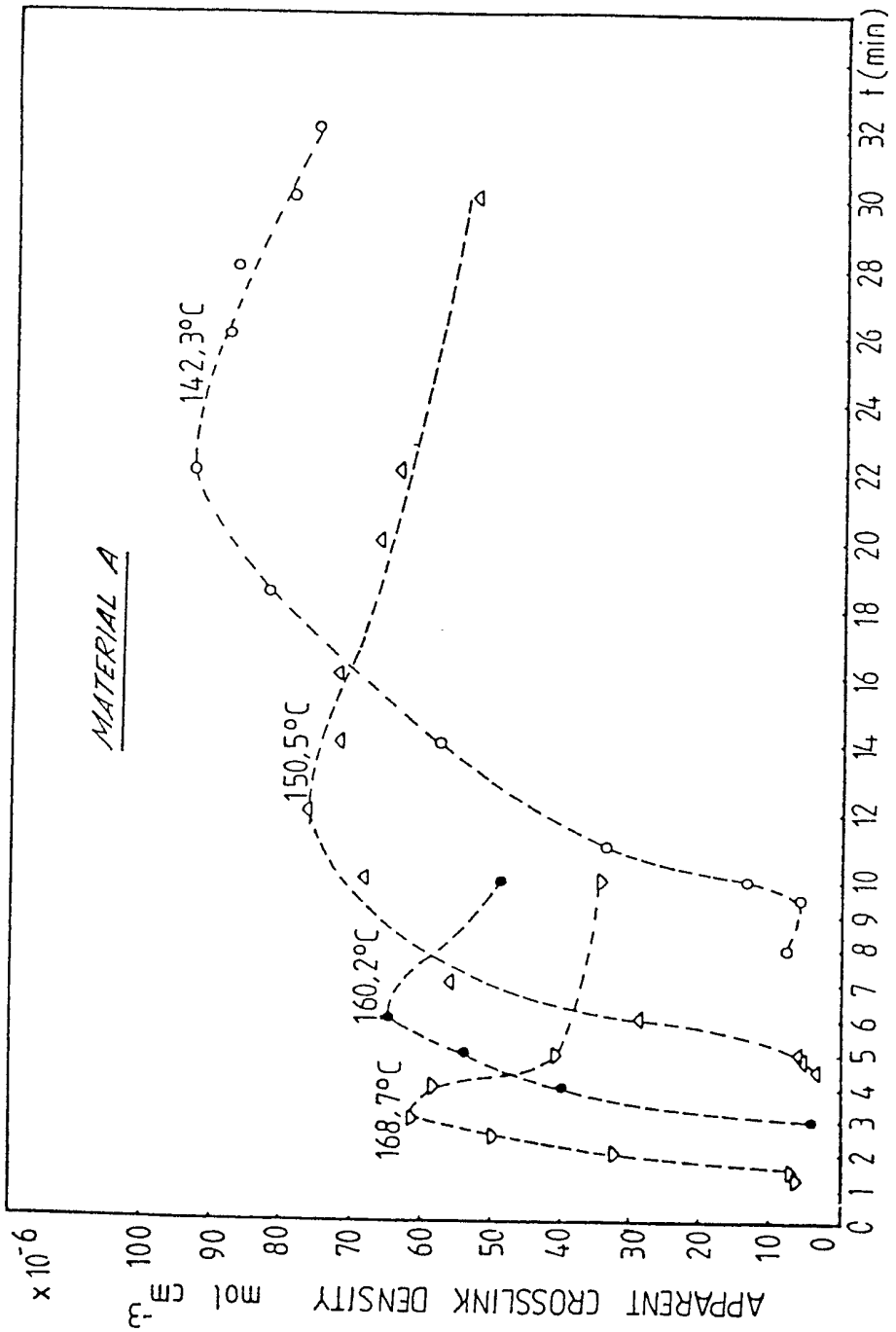

MATERIAL A
142,3°C
150,5°C
160,2°C
168,7°C
APPARENT CROSSLINK DENSITY
x 10⁻⁶ mol cm⁻³
0 10 20 30 40 50 60 70 80 90 100
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 28 30 32 t (min)

FIG.15

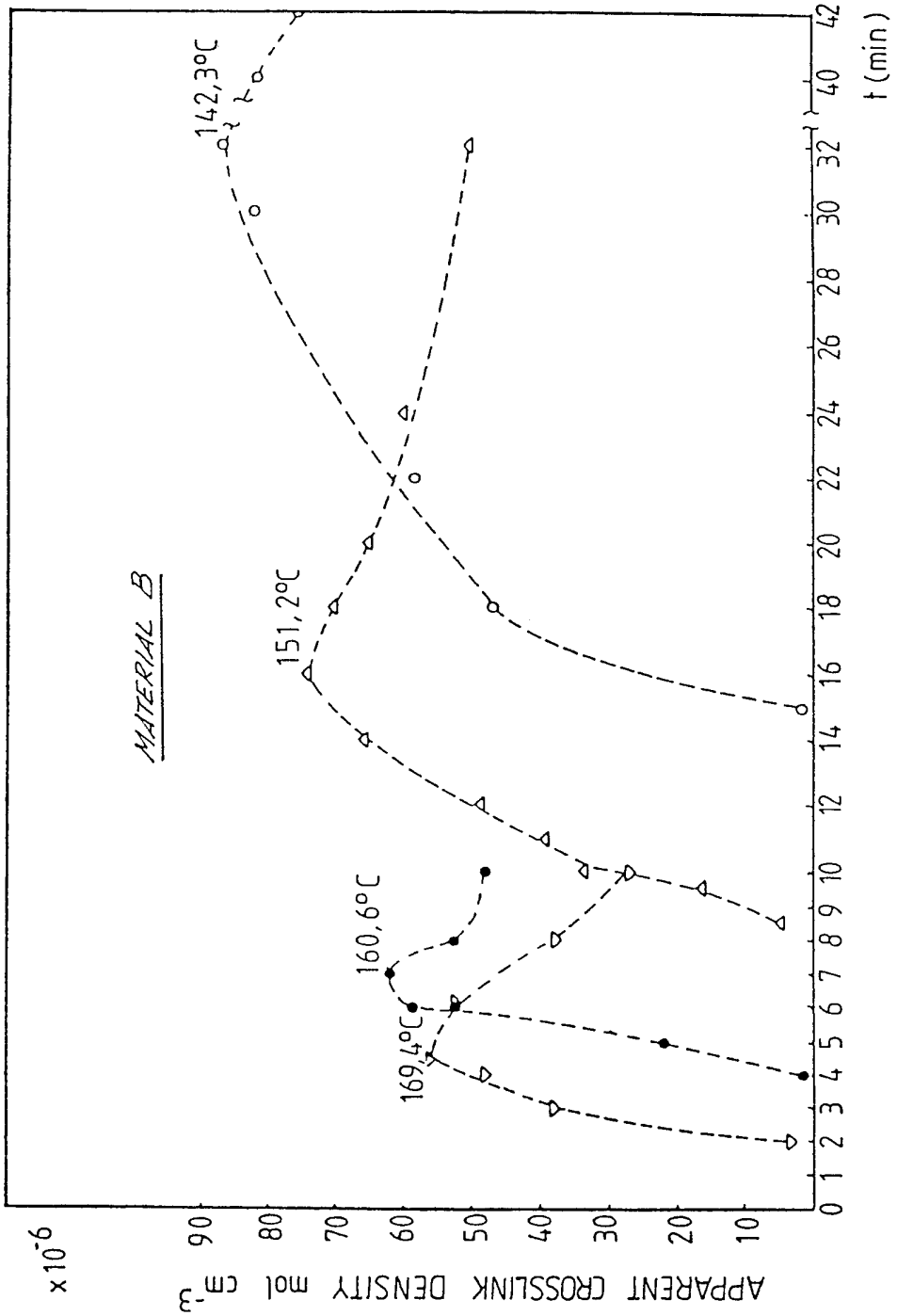

APPARENT CROSSLINK DENSITY mol cm⁻³
x10⁻⁶
90
80
70
60
50
40
30
20
10
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 28 30 32 40 42
t (min)
MATERIAL B
142,3°C
151,2°C
160,6°C
169,4°C

FIG.16

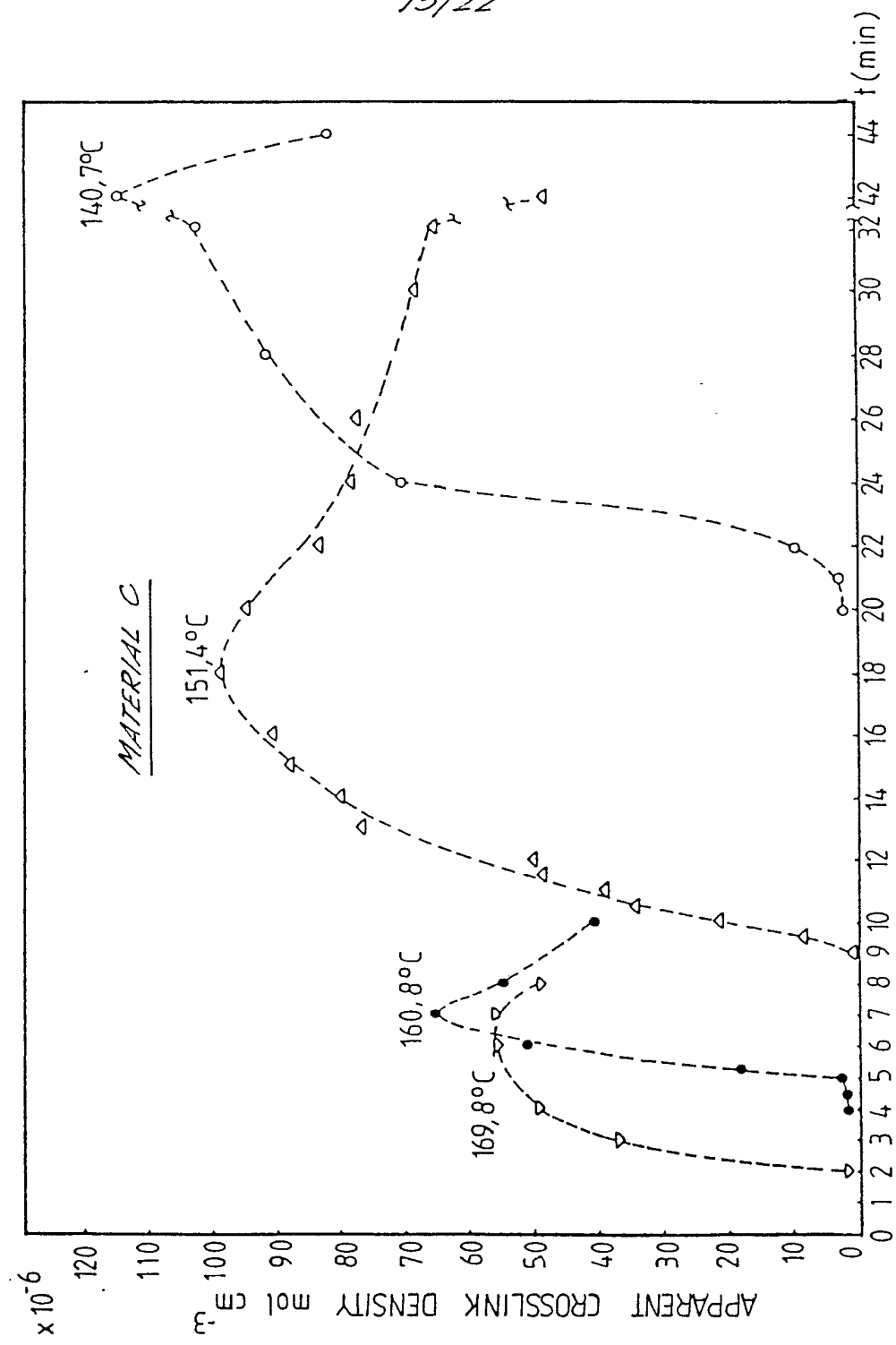

MATERIAL C
140,7°C
151,4°C
160,8°C
169,8°C
APPARENT CROSSLINK DENSITY mol cm-3
x 10-6
t (min)
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 28 30 32 42 44
10 20 30 40 50 60 70 80 90 100 110 120

FIG.17

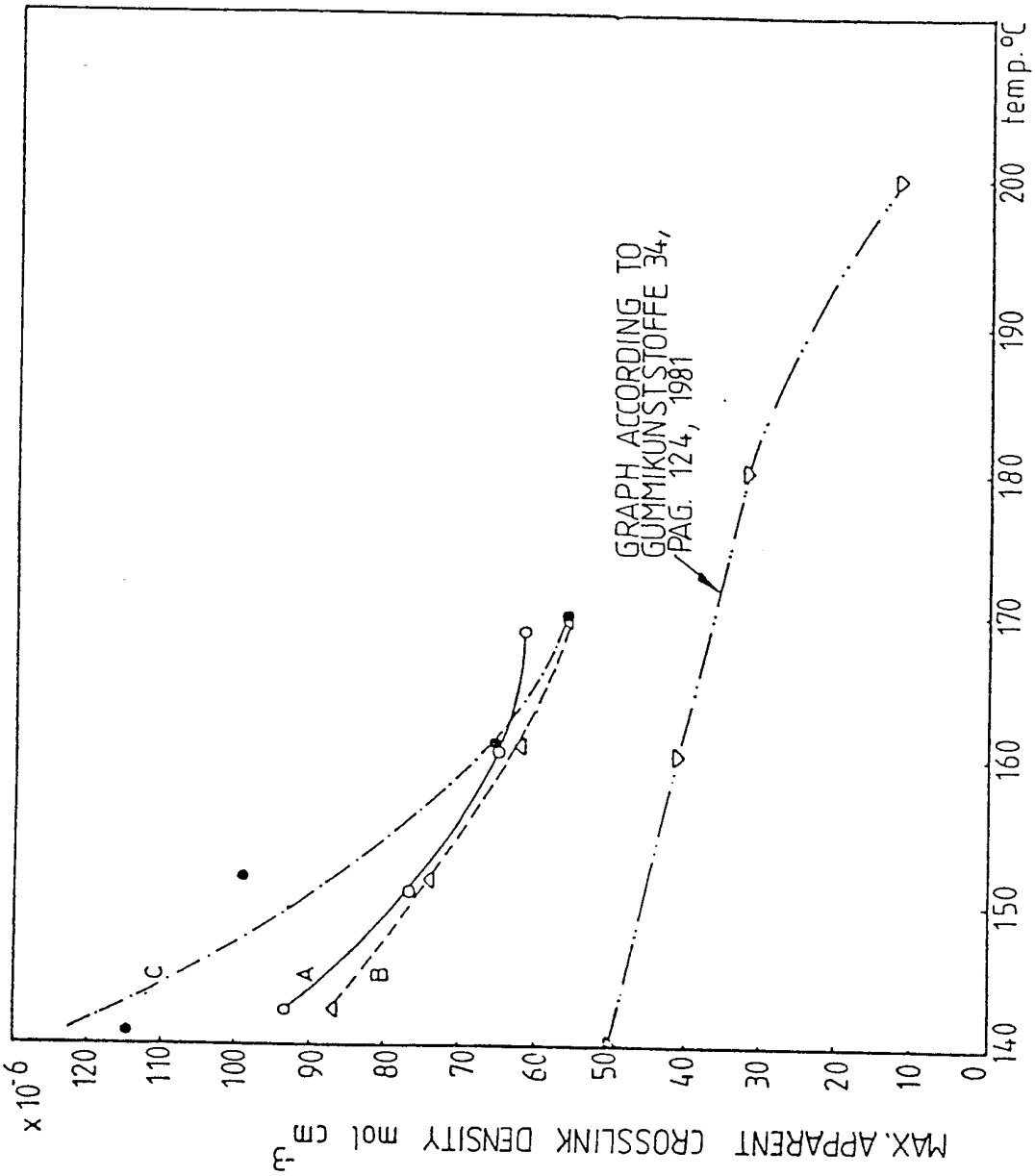
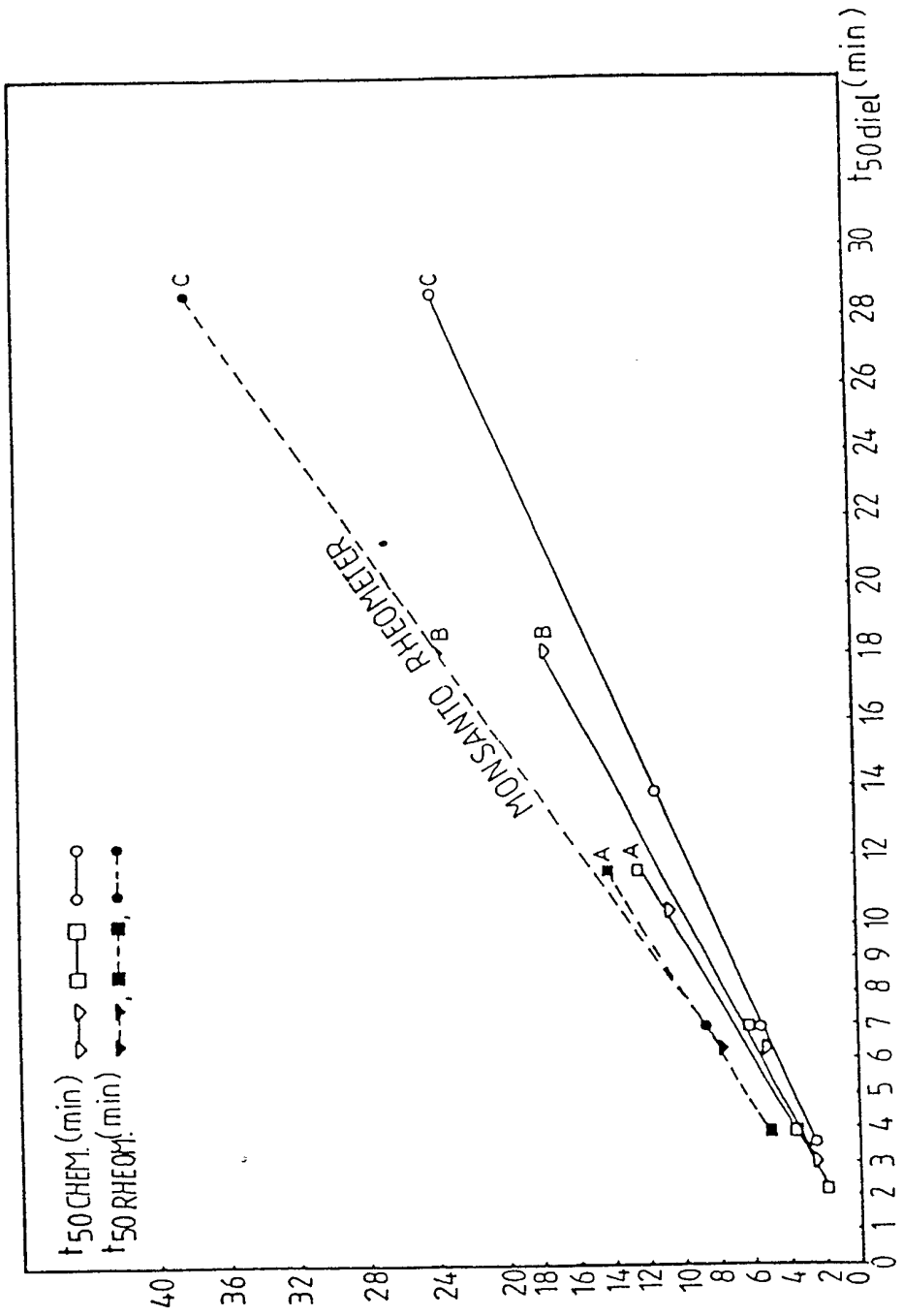

MAX. APPARENT CROSSLINK DENSITY mol cm^{-3}
x 10^{-6}
120
110
100
90
80
70
60
50
40
30
20
10
0
140
150
160
170
180
190
200
temp.°C
A
B
C
GRAPH ACCORDING TO GUMMIKUNSTSTOFFE 34, PAG. 124, 1981

FIG.18


t50 CHEM. (min)
t50 RHEOM. (min)
MONSANTO RHEOMETER
A
B
C
t50diel (min)
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 28 30
0 2 4 6 8 10 12 14 16 18 20 24 28 32 36 40

2187291

FIG.19

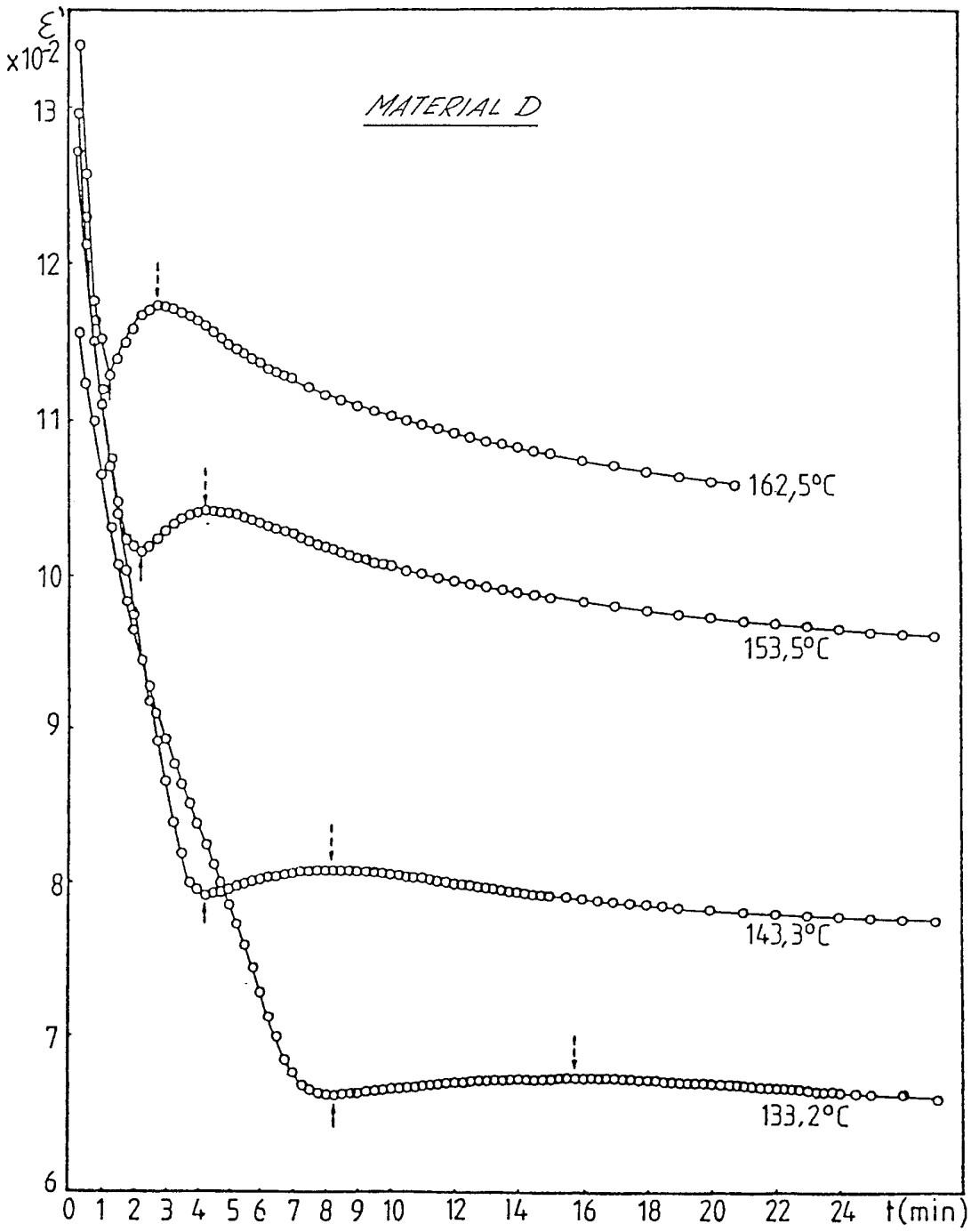


FIG.20

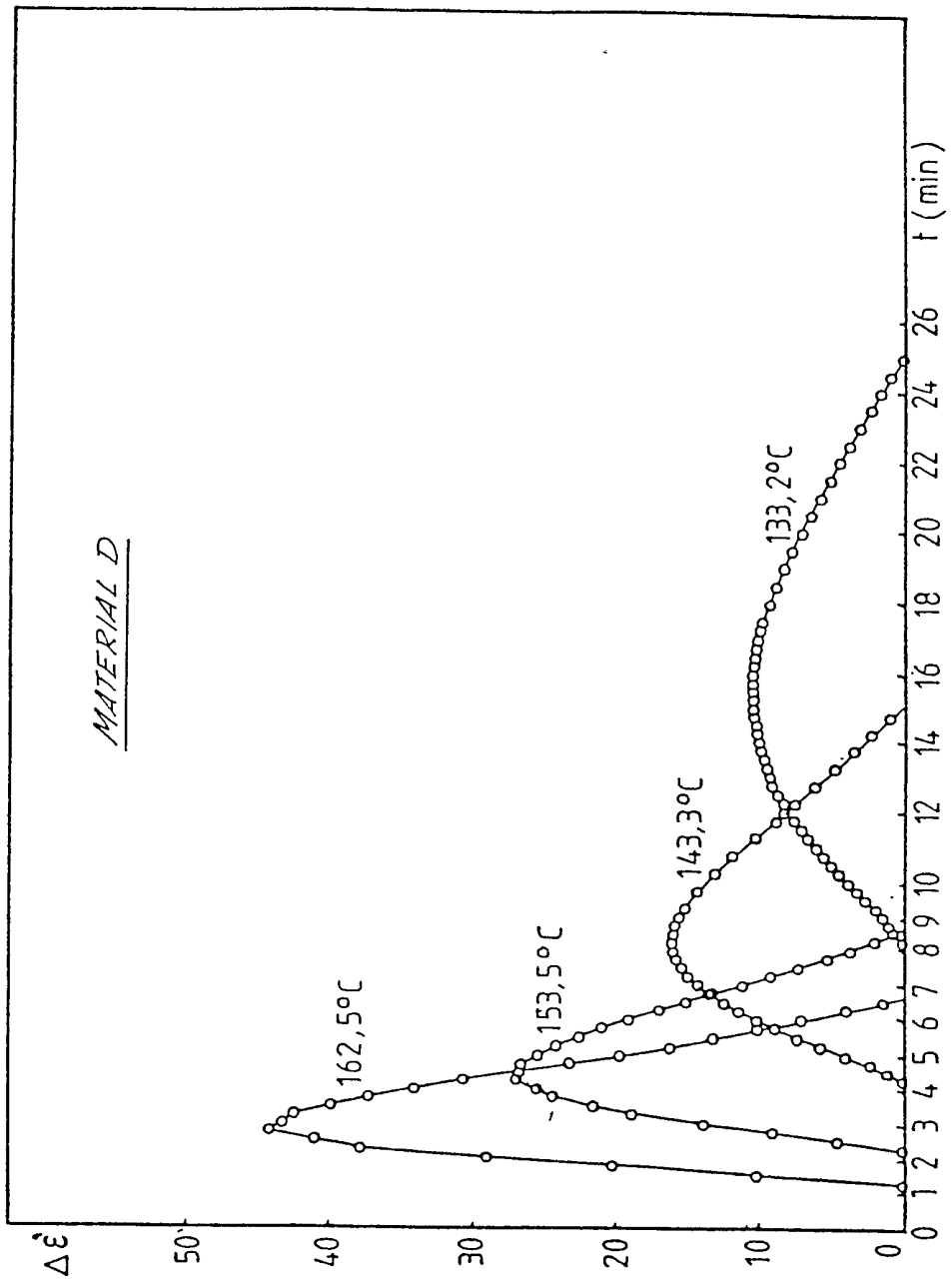

MATERIAL D
Δε'
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 t (min)
162,5°C
153,5°C
143,3°C
133,2°C

FIG.21

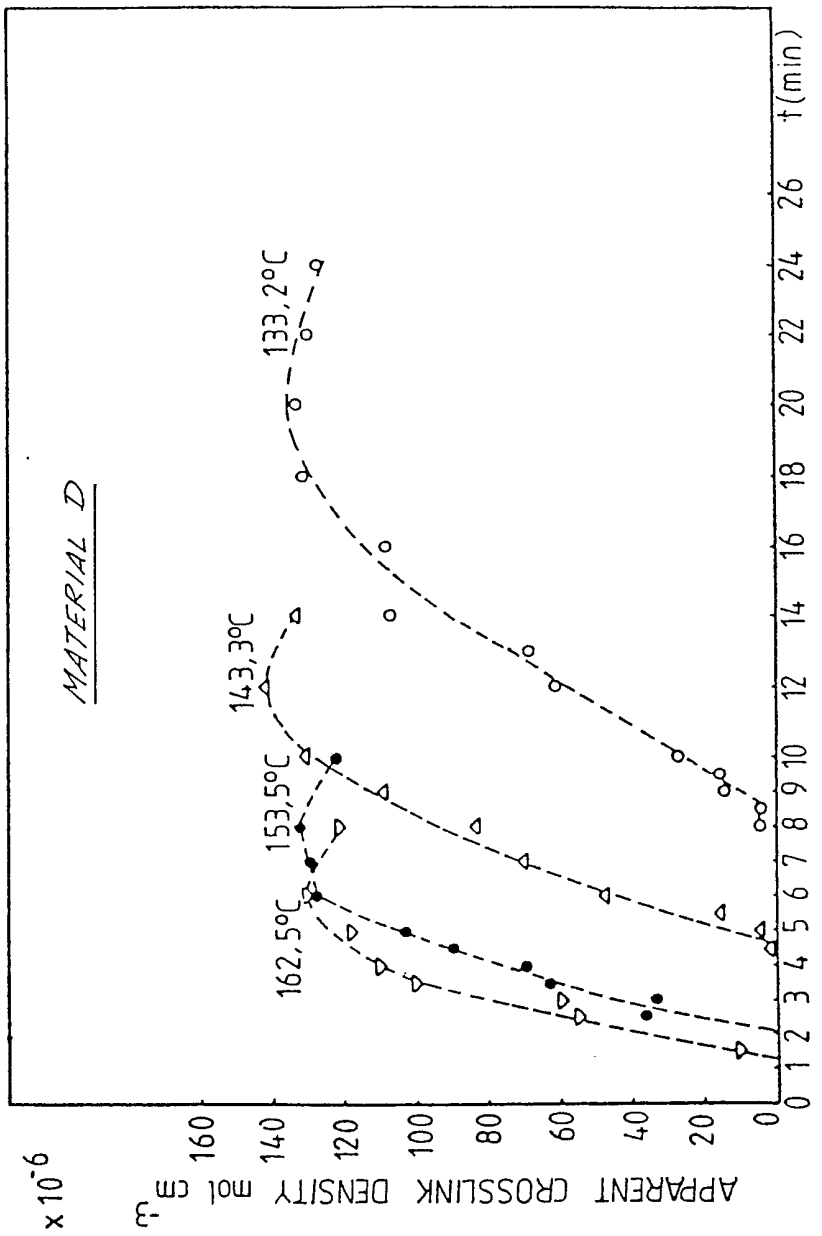

MATERIAL D
APPARENT CROSSLINK DENSITY mol cm^{-3}
x 10^{-6}
0
20
40
60
80
100
120
140
160
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 t(min)
133,2°C
143,3°C
153,5°C
162,5°C

FIG.22

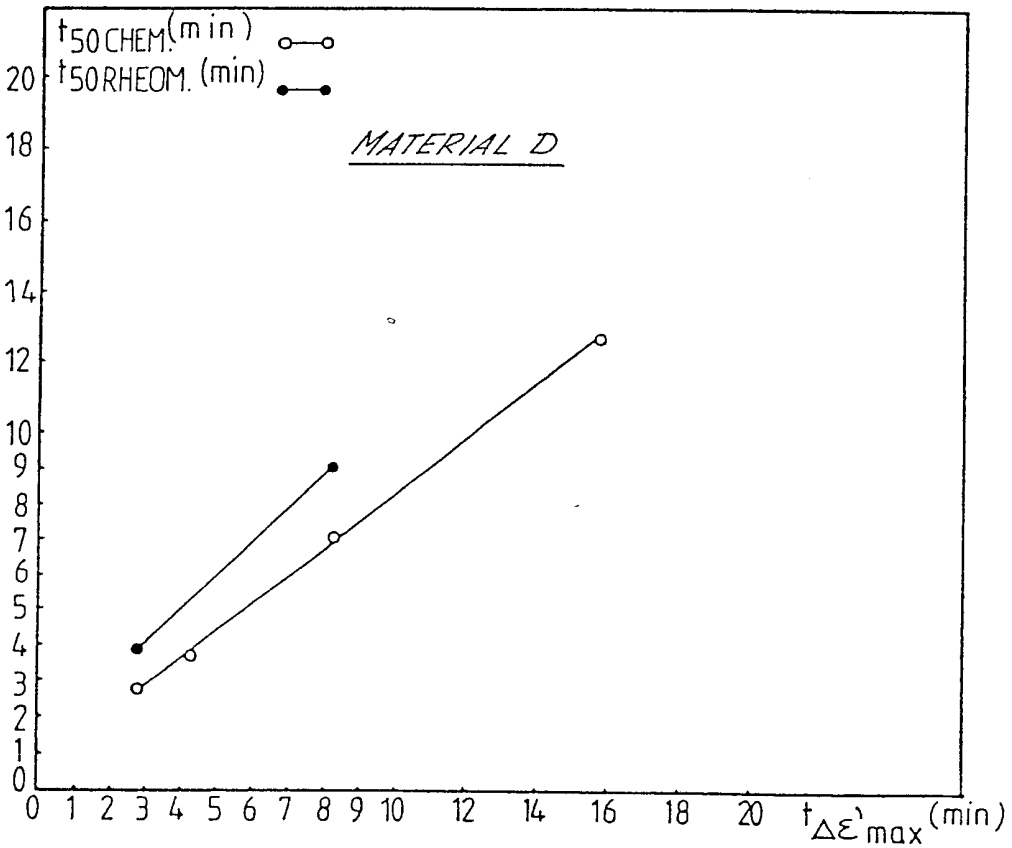
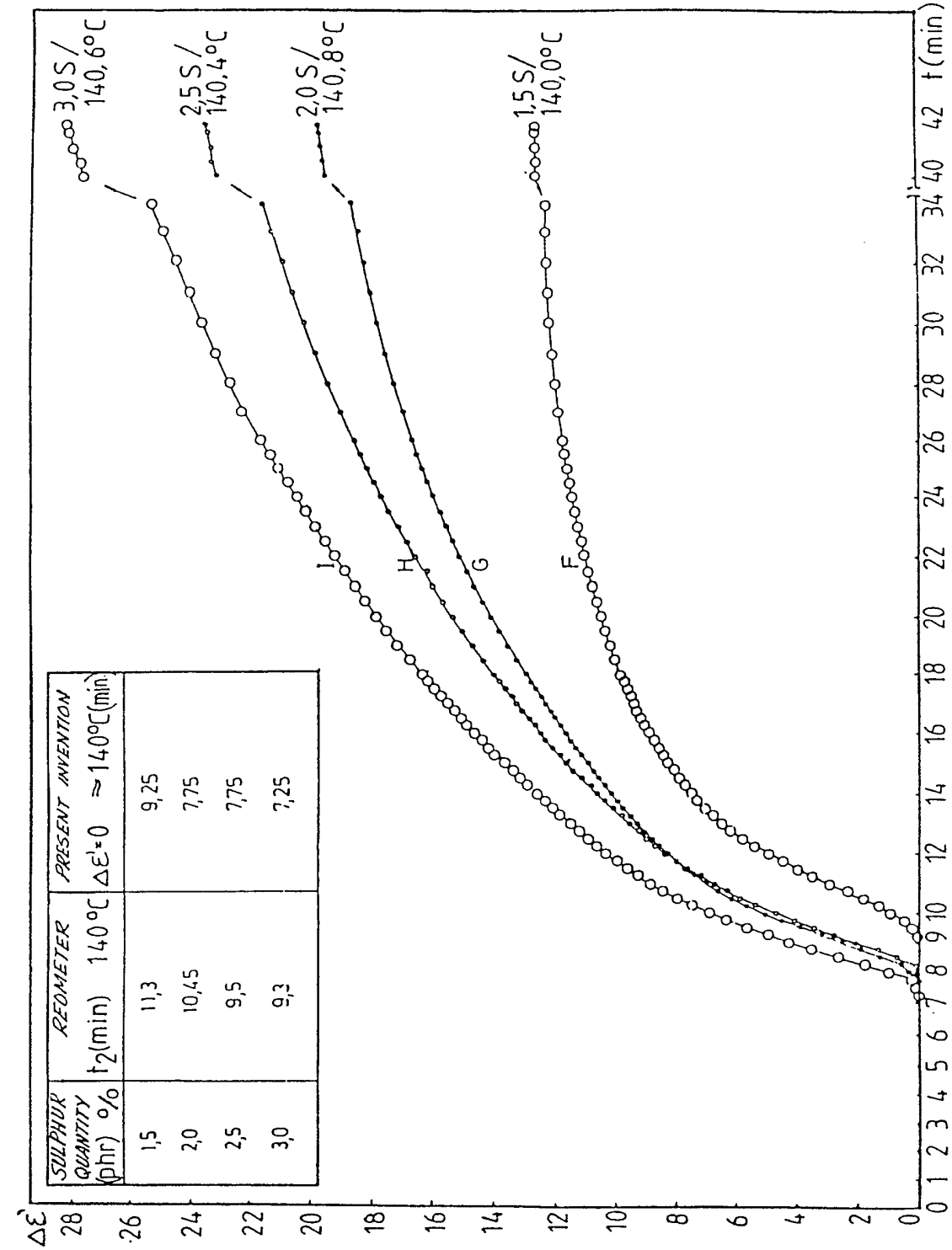
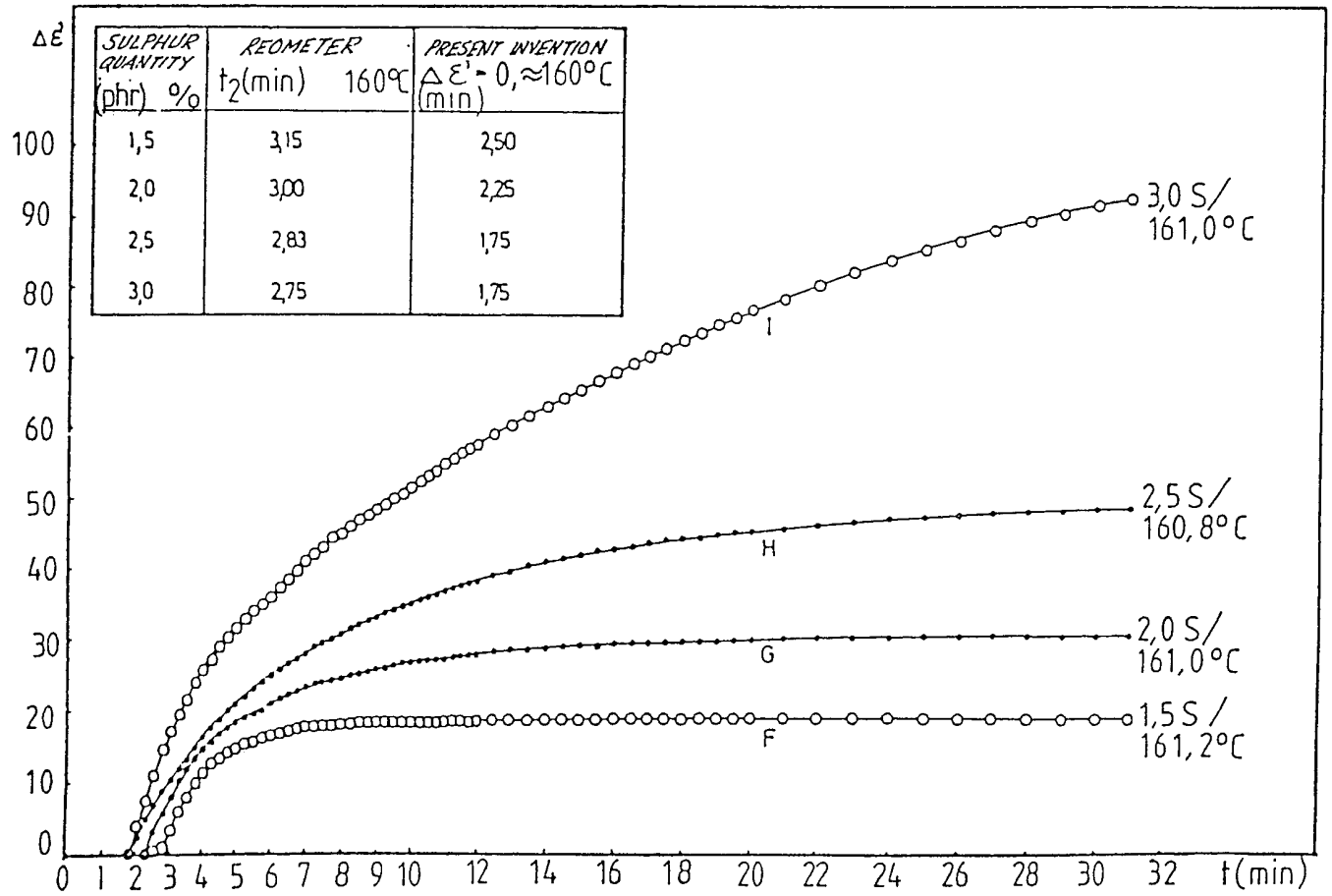

$t_{50\,CHEM.}$(min)
$t_{50\,RHEOM.}$ (min)
MATERIAL D
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20
$t_{\Delta\varepsilon'max}$ (min)

FIG.23



SULPHUR QUANTITY (phr) %	REOMETER t_2(min) 140 °C	PRESENT INVENTION $\Delta\varepsilon' = 0 \approx 140°C$(min)
1,5	11,3	9,25
2,0	10,45	7,75
2,5	9,5	7,75
3,0	9,3	7,25

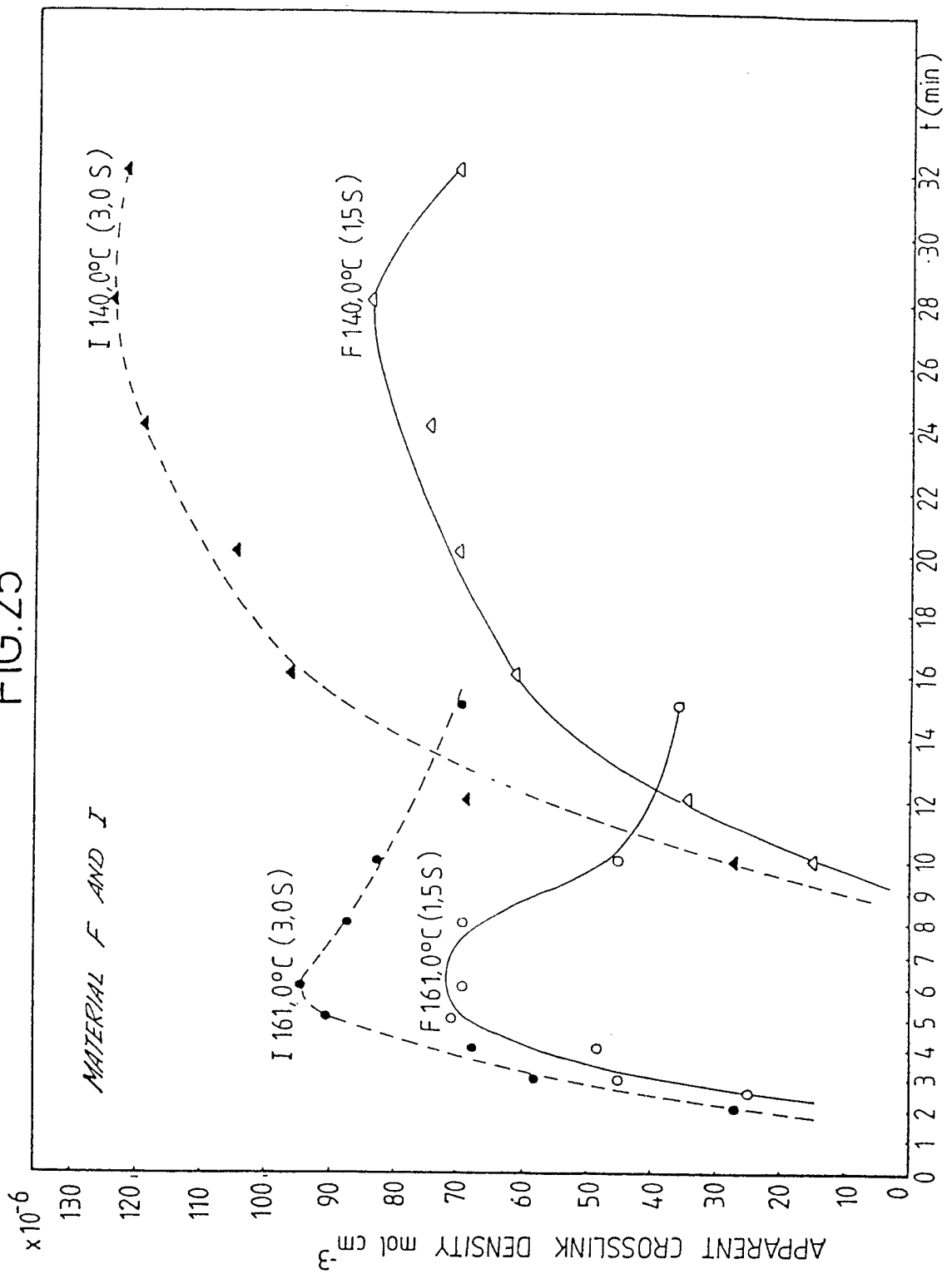
FIG. 24



SULPHUR QUANTITY (phr) %	REOMETER t_2(min) 160°C	PRESENT INVENTION $\Delta\varepsilon' = 0, \approx 160°C$ (min)
1,5	3,15	2,50
2,0	3,00	2,25
2,5	2,83	1,75
3,0	2,75	1,75

2187241

FIG.25


MATERIAL F AND I
I 140,0°C (3,0 S)
F 140,0°C (1,5 S)
I 161,0°C (3,0 S)
F 161,0°C (1,5 S)
APPARENT CROSSLINK DENSITY mol cm⁻³
x 10⁻⁶
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10 12 14 16 18 20 22 24 26 28 30 32 t (min)

SPECIFICATION

A method and an apparatus for determination of basic values

This invention relates to a method for determining basic values from a specimen of a material that is dielectric to analyse its vulcanization characteristics and an apparatus for carrying out the method.

Polymers belong to the group of vulcanizable materials and the electric properties thereof have been the subject of relatively comprehensive studies and research for the major part of this century. These studies and research work have, inter alia, generated a great amount of knowledge of the interior structure of polymeric materials and how this is influenced by admixture of different additives such as plasticizers and organic or inorganic fillers. Dielectric measuring methods have also been used to a certain extent in studies of ageing phenomena of polymeric materials. The control of the vulcanizing or curing processes by means of the changes in the dielectric properties, caused inter alia, by cross-linking or curing reactions, is very rarely used in practice and hardly ever in rubber working technology.

At present the dielectric properties of different polymers are of interest in polymer working substantially only because the dielectric losses can be utilized for generation of heat in connection with preheating or vulcanizing.

Despite the fact that the very earliest work in this special technique, below called vulcametry, was carried out as early as the end of the 1920's the dielectric measuring methods have not yet had any real importance in vulcametry. This can partly be due to the fact that suitable measuring electrodes as well as directly recording measuring bridges have been lacking. However, the most obvious reason seems to be that the basic mechanisms about the influence of the cross-linking reactions on the dielectric relaxation phenomena are not yet known to be used in practical vulcametry.

As is well-known, a dielectric usually contains polarizable or polarized molecules or molecule groups having permanent or induced dipoles. In an electric field the dipoles are oriented in the field direction and molecules containing permanent dipoles show on their part tendencies to orientate themselves in electric fields. How fast and to what extent this orientation takes place has inter alia to do with how the molecules interfere with each other. When a rubber material is vulcanized, or crosslinked, a series of other side reactions, not crosslinkages normally takes place, the other side reactions being characteristic of each combination of rubber and vulcanizing agent. The formation and development of these reactions and reaction products can be followed by the aid of dielectric measuring methods. Thus, the dielectric vulcametry and consequently this invention are based on these changes in the polar properties of the vulcanized rubber.

A method deveolped about 1953 for continuous measurement of the crosslinking reaction in rubber mixtures is described in US patent 3039297. This method can be said to be the start of modern vulcametry and is characterized broadly in that a continuous or periodic motion or force (tensile, compressive, shearing or torsional) is applied to a test specimen of unvulcanized rubber under simultaneous measurement of force and the motion response, respectively. The force/movement is usually transferred to the test specimen by means of a rotor or a linearly movable paddle.

This method was accepted very rapidly and has become very popular generating a long series of different measuring apparatuses, of which the follwing can be mentioned "the Wallace Shawbury Curometer", below called the curometer, "the Cepar-Apparatus", "Viscurometer", "Vuremeo", "Zwick-Schwingelastometer" and the best known of all, viz. the "Monsanto-Rheometer", below called the rheometer.

The original purpose of the technique herein called vulcametry was quite simply to produce a functioning control method in the synthetic rubber industry which grew rapidly in the post-war period. Vulcametry has thereafter also been found to be a very useful method for study of the reaction kinetics of the vulcanization process and has also been used for this purpose. However, in later years some criticism has been directed to this so-called traditional vulcametry which can be said to be mechanical. Inter alia it has been shown that the test specimen is heated relativley slowly and even after reaching the temperature of equilibrium there are temperature gradients through the test specimen, that a non-desired sliding can arise between cavity and rotor and paddle, respectively and that certain rubber materials have a tendency to become porous during the testing procedure.

Certain comparative studies with isothermal vulcanization which are considered to give acceptedly true values and are described in Polymer Testing Vol. 1, No. 4, page 247, 1980 by R H Norman, have also shown that the curometer which, in turn, gives longer vulcanization times than isothermal vulcanization, and examples of this appear from the table below indicating 90% of vulcanization time in seconds at different temperatures.

Temperature °C	Isothermal vulc.	Curometer	Rheometer
120	3120	4800	7800
140	870	1100	1800
160	280	320	460
180	72	105	195
200	17	47	97

The great differences at low temperatures apparent from the table are unexpected and are probably due to the fact that there is a considerable difference between the true average temperature of the test specimen and the measured temperature even after a very long period of time. On the other hand, the great difference at high temperatures is not entirely unexpected. It has been shown that the rheometer in comparison with guaranteed isothermal conditions gives vulcanizing times that are about twice as long at most temperatures. There are two probable explanations of these substantial deviations. Firstly, heat is continuously lost as heat is diverted from the rotor via the rotor shaft to the drive unit of the rheometer, with the result that the rotor becomes colder than the rotor cavity. Due to this the average temperature of the rubber specimen will be considerably lower than the adjusted temperature and therefore the vulcanization process will proceed more slowly. Secondly, it will take a longer time to heat the specimen in a rheometer in comparison with the conditions prevailing when producing the isothermal results shown in the above table due to the fact that the test specimen in the rheometer is much thicker than 0.5 mm which is the thickness of the specimen used in the isothermal tests.

Another disadvantage of conventional vulcametry is the interpretation problems arising when data produced by the rheometer are to be used to determine vulcanization times of voluminous rubber products such as big rubber dampers, contract tyres, mill linings etc. Therefore there is a great demand for a method or process enabling measurement of the vulcanization course directly during the vulcanization of these products.

It would therefore be desirable to provide a method, and an apparatus for carrying out the method, enabling measurement of the vulcanization course directly during the vulcanization in a quick and safe manner and giving true measured values as a result.

Accordingly the present invention provides a method for determining basic values of a material specimen for analysis of its vulcanization characteristics, wherein the specimen is shaped under pressure and at a temperature preferably in excess of 100°C to a predetermined form and thickness between two electrodes having plane-parallel sides facing each other which are brought into intimate contact with the shaped body during shaping in order to form a cpaacitor whereafter the basic values being the capacitance (C) and loss angle (D) of this capacitor and the temperature of at least one of the electrodes, are measured and recorded simultaneously.

In a preferred embodiment the specimen is shaped in a cavity, having the requisite predetermined form and thickness provided, in a specimen carrier made from an electrically non-conductive material and having plane-parallel sides which is placed between the electrodes, more preferably the specimen carrier is heated to the intended temperature before the specimen is placed in the cavity thereof to be shaped.

In a particularly preferred embodiment the predetermined thickness of the specimen is less than or equal to 1 mm and preferably less than or equal to 0.25 mm. The capacitance (C) and loss angel (D) may be measured by means of an impedance analyzer and the temperature of the electrode plates by means of a thermoelement connected to a digital thermometer with an analog output.

A second embodiment of the present invention provides an apparatus for the determination of basic values of a material specimen for the analysis of its vulcanization characteristics, which comprises two electrodes having plane-parallel sides facing each other and which are adapted to be heated to temperatures preferably in excess of 100°C and adapted to compress a material specimen placed between them to a predetermined shape and thickness in order to, by intimate contact with the body shaped from the specimen, form, together with the body a capacitor, a means connected to the electrodes for measuring the capacitance (C) and loss angle (D) of the capacitor and a temperature sensing means connected to at least one electrode for determining the temperature, the means for measuring temperature, capacitance and loss angle being connected to a unit adapted to record the resulting values as basic values.

Preferably the electrodes are supported by platens included in a press and galvanically separated therefrom.

Preferably the temperature sensing means comprises a thermoelement and a digital thermometer with an analog output, the thermoelement being connected to and galvanically separated from the electrode.

In a preferred embodiment the apparatus further comprises a specimen carrier of an electrically

non-conductive material and having plane-parallel sides which is adapted to be located between the electrodes and to enclose in a cavity of requisite predetermined shpae and thickness the material specimen during its shaping and vulcanization.

The platens (2) of the press may also be heat plates for heating the electrodes, and consequently the specimen carrier and the material specimen to the intended temperature, the heat plates being connected to their respective temperature regulators for adjusting the temperature.

The unit recording the basic values may preferably be a 3-pen writer

In principle it can be said that the aim of the method is to measure the relative permittivity ε'_r and and dielectric loss factor ε'' of the rubber as a function of the time at a frequency of at least 10 kHz and preferably at a higher frequency, for instance in the range of from 200 to 300 kHz, while rubber is vulcanized at an elevated temperature, preferably in the range of from 120 to 190°C.

Preferred embodiments of the invention are described in greater detail below with reference to the accompanying drawings, in which:–

Figure 1 shows schematically an apparatus according to the invention for carrying out the method;

Figure 2 is a plane view of a specimen carrier according to the invention;

Figure 3 shows examples of structures formed between molecule chains during vulcanization;

Figure 4 shows a circular, plane-parallel capacitor of the type obtained in a method of the invention;

Figure 5 shows an equivalent diagram or circuit of the capacitor;

Figure 6 shows how dipoles and ions orientate themselves in a material to which an electric voltage has been applied;

Figure 7 shows an equivalent diagram of a capacitor containing a dielectric having a high leakage and a tendency to form blocking layers;

Figures 8–13 show different curves, that is to say so-called dielectric curo- or vulcograms, of ε' or $\Delta\varepsilon'$ as a function of the time at different temperatures and frequences for different rubber mixtures; and

Figures 14–25 show additional curves for illustrating the invention, these curves being defined in more detail hereinafter.

The vulcanization process does not in general proceed as a simple chemical reaction but consists of a series of complex reactions that may require hours to complete to form certain bonds.

Sulphur and substances giving off sulphur are not the only chemical substances participating in these reactions; other substances such as metal oxides, fatty acids and organic accelerators also take part actively in the crosslinking reaction. The organic accelerators do not operate as normal catalysts that do not participate actively in the vulcanzing reaction. The main task of the accelerators is to activate the sulphur and, as distinguished from normal catalysts, the accelerators undergo chemical changes.

Accelerated sulphur vulcanization is generally considered to proceed according to the following steps:

a/ the accelerators react with sulphur forming monomeric polysulfides Ac-S_x-Ac where Ac is an organic radical formed from the accelerator.

b/ The polysulphides can react with rubber forming polymeric polysulphides of the following structure; rubber-S_x-Ac.

c/ The polymeric polysulphides either react directly or via intermediates forming polysulphidic crosslinkages between the rubber molecules according to: rubber-S_x-rubber.

Examples of the multiplicity of structures formed between the molecule chains (intermolecularly) and within one molecule chain (intramolecularly) appear in Fig. 3.

In the general case shown in Fig. 3 not only (a) mono-, (b) di-, and (c) polysulphidic crosslinkages are formed in diene rubbers (i.e. rubbers containing conjugated double bonds) but also (d) sulphidic groups with accelerator fragments in side position, (e) intramolecular cyclic mono- and (f) disulphides, (g) conjugated dienes and (h) trienes, (i) parallel adjacent crosslinkages, (j) crosslinkages bonded to the same or adjacent carbon atoms, (k) C–C bonds (which probably do not exist) and (1) material which is not crosslinked.

In vulcanization the poly- and disulphidic crosslinkages formed initially undergo a series of maturation reactions.

The polysulphidic crosslinkages and the laterally positioned polysulphidic groups undergo desulphurizing reactions to be reformed to di- and gradually monosulphidic crossslinkages and groups.

Before the final formation of the thermally stable monosulphidic crosslinkages and groups takes place the di- and polysulphidic crosslinkages can undergo thermal reactions, sulphurous products, such as cyclic sulphides, being formed.

Several of the reactions between sulphur and substances giving off sulphur described above increase the polarity of the network formed. These polar groups, their formation and changes during vulcanization reactions are utilized in accordance with the principles on which the inven-

tion is based to study the vulcanization.

According to one embodiment of the invention illustrated in the Figures the apparatus for these measurements and consequently for determining the required basic values from a specimen of a vulcanizing material to be analyzed comprises a press 1 having a press pressure of at least 200 kPa and two platens 2 which can be heated and the temperature of which is adjusted by means of a temperature regulator 3 for each. Each platen or heat plate 2 is provided with an electrode plate 4 of aluminium galvanically separated from the associated heat plate 2 by means of a layer 5 of teflon (R.T.M.) foil. This layer 5 need not be thicker than 1mm. To the upper electrode plate 4 a thermoelement 6 is connected by means of which the temperature of the electrode plate is measured and the tip of which is placed at a small distance, for instance 0.3 mm inside the surface of the electrode plate. The thermoelement 6 is galvanically separated from the electrode plate 4 by means of a very thin coating of silicone rubber and is connected to a digital thermometer 7 with analog output which, in turn, is connected to the temperature input T of a 3-pen writer 8.

Moreover, each of the electrode plates 4 is connected to an impedance analyzer 9 means of which capacitance C and loss angel D (tan δ) are determined and which can have a frequency range between 5 Hz and 13 MHz. The impedance analyzer 9 is connected with its ouputs to the capacitance input C and loss angle input D of the 3-pen writer.

A specimen carrier 10 consisting of a ring 11 provided with a handle of for instance teflon (R.T.M.) i.e. an electrically non-conductive material and with an opening or measuring cavity 12, the volume of which is defined and in which the material specimen is placed after introducing the specimen carrier 10 between the electrode plates 4 of the press also belongs to the apparatus.

In order to achieve the best possible measuring result in the shortest possible time the material specimen should have the smallest possible volume and thickness and this is also obtained in accordance with the invention thanks to the fact that the specimen carrier can be made very thin, even thinner than 0.25 mm. The measuring cavity 12 of the specimen carrier shown in Fig. 2 has for instance a volume only amounting to 0.28 cm^3 and with predetermined volume of the measuring cavity 12 it is also relatively simple to determine, for instance by weighing, the size of the material specimen so that it will fill up the measuring cavity 12 exactly in pressing.

In accordance with the invention the empty specimen carrier 10 is placed between the heated electrode plates 4 of the open press 1 after which the press 1 is closed and kept closed until the test specimen 10 has been heated to the current testing temperature. After only a few seconds the specimen carrier 10 will take the temperature of the electrode plates 4, and thereafter the press 1 is opened and a material specimen prepared in advance is placed as fast as possible on the lower electrode plate 4 and as centrally as possible within the measuring cavity 12 of the specimen carrier. The press 1 is thereafter closed again and air pressure is rapidly increased to the intended value, for instance 200 kPa, which has been found to be sufficient to press out the specimen consisting of unvulcanized rubber so that this will fill up the measuring cavity 12 of the specimen carrier enclosed by the electrode plates 4 completely at the same time as it prevents porosity from arising in the specimen. Thanks to the fact that the pressed-out specimen becomes very thin, for instance 0.25 mm, it is heated very rapidly, i.e. within less than half a second, a time that is so short that it can be completely neglected in comparison with the normally current vulcanization times. As soon as the press has closed the capacitance values C, tangent δ-values D and temperature values T start start to be automatically recorded by the 3-pin writer 8.

Thus, these values derive from the body of vulcanized rubber located within the specimen carrier 10 which body forms together with the two electrode plates 4 a circular, plane-parallel capacitor 13 (Fig. 4), the relative permittivity ε'_r and dielectric loss factor ε'' of which can be easily calculated by means of the resulting values of capacitance and loss angle. It should be noted that no separation films have been used between the electrode plates 4 and the dielectric (the vulcanized rubber) and this is an advantage as such films have been found to give measuring results that are strongly influenced whether the film is charged or discharged through the bulk resistance of the dielectric.

As is well-known, the capacitance of a plane-parallel capacitor of the type for instance shown in Fig. 4 is decided by the surface A of the electrode plates and their mutual distance L. A capacitor thus consisting of two electrode plates with the surfaces A having a mutual distance L and containing a homogeneous dielectric, the vulcanized rubber in this case, with the relative permittivity ε'_r and loss factor ε'' can be described by means of an equivalent diagram or ciruit 14 of the type shown in Fig. 5. This circuit is built of the capacitance C_p which is connected in parallel with the resistance R, and the capacitance C_p and the resistance R can be written

$$C_p = \varepsilon_o \varepsilon'_r \frac{A}{L}; \quad \varepsilon'_r = C_p / C_o \qquad \text{Equ. (1)}$$

$$R = \frac{L}{w \times A \times \varepsilon'' \times \varepsilon_o} \qquad \text{Equ. (2)}$$

where

ε_o = the vacuum permittivity
w = the angular frequency
C_o = the capacity of an empty capacitor
C_p = the capacity of a capacitor containing a dielectric.

By reforming the equations (1) and (2) explicit expressions of ε'_r and ε'' are obtained.

$$\varepsilon'_r = \frac{C_p \times L}{A \times \varepsilon_o} \qquad \text{Equ. (3)}$$

$$\varepsilon'' = \frac{L}{ARw\varepsilon_o} \qquad \text{Equ. (4)}$$

It is apparent from the equations (3) and (4) that the relative permittivity ε'_r is not actuated by the resitive component R which ε'' is influenced.

Polymers in general and polymers in particular containing electrically conductive substances such as carbon black can transport charges if an electric voltage is applied across the material (the dielectric), see Fig. 6.

The resistivity of a dielectric and its tendency to form blocking layers at the surfaces of the electrode plates influence the dielectric properties of the material. Dielectrics having a low resistivity are said to have a high leakage.

The equivalent diagram of a capacitor containing a dielectric with a high leakage and having tendencies to form blocking layers is apparent from Fig. 7.

The part of the resistance (R_{DC}) caused by charge transport is independent of the frequency of the electric field applied across the capacitor as distinguished from the part of the resistance (R_p (W)) caused by the dipolar relaxation. If the current through a dielectric is caused by charge migration the resistance of the dielectric can be characterized by it bulk resistivity. The two charged layers formed at the surfaces of the electrode plates have in Fig. 4 been combined to a blocking capacitor C_b which is connected in series with the circuit connected in parallel formed by C_p, R_p (w) and R_{DC}.

The loss equation ε'' can then be written

$$\varepsilon'' = \frac{1}{wC}\left(\frac{1}{R_{p(w)}} + \frac{1}{R_{DC}}\right) = \frac{1}{Aw}\left(\frac{1}{R_{p(w)}} + \frac{1}{R_{DC}}\right) \qquad \text{Equ. (5)}$$

R_{DC} being the resistance caused by charge transport and $R_{p(w)}$ being the resistance caused by the dipolar relaxation.

The dipolar parallel resistance $R_{p(w)}$ goes towards infinity when the frequency goes towards zero while ε'' will increase due to the D.C. conduction when the frequency decreases.

If the conductivity of the dielectric is so high that the impedance of R is less than the impedance R_c of C

$$R_c = \frac{L}{wA\varepsilon'_r\varepsilon'_o} \qquad \text{Eqv. (6)}$$

$\varepsilon''\varepsilon'$ will be $\tan\delta > 1$ resulting in that the charge of C_b through R will dominate the electric behaviour of the circuit.

The electrode polarization, i.e. the charge of C_b, will *not* influence the characteristic of the electric cirucit as long as R is greater than R_c. It can be concluded from this that electrically isolating separation films between the dielectric and the electrode plates, which sometimes have been used in similar connections, should not be used so that these films disturb or usually make

correct measurements completely impossible.

The function of the present method and how the measurement results obtained correlate with the corresponding ones from other known and established measuring methods is described in more detail in the following by the aid of some examples.

Example 1

The method of the invention is applied to natural rubber mixtures A, B and C with conventional sulphur/accelerator systems and retardants (Santogard PVI-50) and having a composition according to the following table 1:

	A	*B*	*C*	*D*
NR SMR CV 60	100	=	=	=
Carbon black N220	45	=	=	=
Dutrex 729 HP[1/]	8	=	=	=
ZnO	4	=	=	=
Stearic acid	1	=	=	=
TMQ[2/]	1.5	=	=	=
6 PPD[3/]	1.5	=	=	=
Microcrystalline wax	2	=	=	=
CBS[4/]	0.8	=	=	
Sulphur	2	=	=	
PVI-50[5/]	—	0.5	0.8	
TMTD[6/]				1
DTDM[7/]				1

[1/] Aromatic oil
[2/] Pol trimethyl-dihydrochinoline
[3/] Dimethylbutyl-phenyl-p-phenylene diamine
[4/] N-cyclohexyl-2-benzothiazyl-sulfenamide
[5/] Cyclohexylthiophthalimide CTP
[6/] Tetramethylthiuram disulfide
[7/] 4,4'-dithiomorpholine

The mixtures shown in the table are typical of such mixtures of natural rubber used in industry for the manufacture of for instance automobile tyres. The mixtures A, B and C are identical except for the fact that the mixtures B and C contain small amounts—0.5 phr and 0.8 phr, respectively—of a retardant (Santogard PVI-50) moving the start of the vulcanization towards longer times. The mixture D is also identical to the mixture A except for the fact that the conventional sulphur/accelerator vulcanization system in mixture A has been exchanged for an accelerator/sulphor donor vulcanization system. Such systems are generally designated EV-(Efficient vulcanization) systems.

On the basis of the basic values obtained by means of the method and apparatus of the invention different curves can be obtained and a number of such curves is shown in Figs. 8–24. In the following some of these curves are called dielectric curo- or vulcograms showing ε'_r as a function of the time at different temperatures and frequencies and for the mixtures A, B and C such curograms are shown in Figs. 8, 9 and 10.

The dielectric curograms of the mixtures A, B and C all have the same form in the sense that ε'_r decreases initially and starts to increase again via a minimum poiunt ($\varepsilon'_{r\,min}$). The time up to $\varepsilon'_{r\,min}$ is as well as being dependant on the temperature, also dependent on the composition of the mixture in such a way that a high temperature gives shorter times to $\varepsilon'_{r\,min}$ and that ther retarded mixtures (B and C) give longer times to $\varepsilon'_{r\,min}$ than the non-retarded mixture A.

To find inflection points dependent on temperatures, frequency and retardance in the dielectric curograms was unexpected considering the fact that the measuring cavity 12 is filled with a material—a dielectric—having a relative permittivity $\varepsilon'_{r\,min}$ being in the range of 500 to 1900 depending on temperature and frequency.

As the capacitance of a plane-parallel capacitor, as previously mentioned, is proportional to the surface area, of the dielectric and inversely proportional to its thickness it is very important that the geometric form of the dielectric is kept constant. Sometimes this has been relatively diffiult to accomplish as a small displacement of the positon of the rubber specimen in the specimen carrier 10 and small variations of the weight of the specimen may cause the rubber to flow asymetrically in the specimen carrier 10 with the result that part of the rubber will flow out of the specimen carrier on one side at the same time as a waste is formed on the other side or that the specimen carrier is filled either too much or too little. The effect of this is that both the surface and the thickness of the dielectric can vary a little if very much care is not taken on preparation and placement of the specimen in the specimen carrier 10.

If an analysis method, especially one that is intended for routine analysis is to be acceptable it is necessary that the preparation of the specimen should be simple. To avoid the problem with the ε'_r-values being displaced due to the fact that the size and thickness of the dielectric may vary a little the measured values can be normalized in the following way. Instead of using absolute values of ε'_r,$\Delta\varepsilon'_r$-values can be calculated by subtracting the lowermost ε'_r-value, i.e. the ε'_r-value at the inflexion point, from all following ε'_r-values.

$\Delta\varepsilon'_r = \varepsilon'_r$ $t \geqslant t$ inflex. $-\varepsilon'_r$ inflex. Equ. (7)

$\Delta\varepsilon'_r$ is then plotted as a function of the time.

In Figs. 11, 12 and 13$\Delta\varepsilon'_r$ values calculated according to equ. (7) for the mixtures A, B and C from data recorded at 300 kHz have been plotted as a function of the time at four different vulcantization temperatures.

For the mixtures A, B and C vulcanized at about 140, 150 and 160°C the $\Delta\Sigma_r$-values increase monotonously, especially at the lower vulcanization temperatures. Higher vulcanization temperatures always give higher initial inclination of the $\Delta\varepsilon'_r$-curves than lower temperatures which shows that the inter- and intra-molecularly bonded sulphur gives a chemical structure of the network that becomes more polar the higher the vulcanization temperature is.

At about 170°C $\Delta\varepsilon'_r$ increases for the mixtures B and C initially to decrease again via a maximum. At present it is not known why mixture A does not show the same behaviour as B and C at about 170°C. The reason may possibly be that the retardant Santogard PVI-50 included in the mixtures B and C influences the chemical structure of the network.

In order to investigate what is the correspondence of the inflection points in the curograms in Figs. 8, 9 and 10 or the zero-values ($\Delta\varepsilon'_2 = 0$) in Figs. 11, 12 and 13 in the vulcanization of the test specimens, a great number of specimens is vulcanized at the temperatures used for recording the dielectric curograms. Part of the specimens was vulcanized for a somewhat shorter time or the same time as the corresponding time necessary to reach to ε'_r-minimum or the time to reach $\varepsilon'_r = 0$. A larger number of test specimens was vulcanized for longer times than the time necessary to reach the ε'_r-minimum. The cross linkage density of the specimens was determined by swelling the specimens in dichlorotmethane for 6 days at room temperature, after which the crosslinkage density was calculated by means of Flory-Rehner's equation. The influence of the carbon black on the crosslinkage density has been compensated by means of correction factors which are well known in the art.

The change of the crosslinkage density as a function of the vulcanization temperature and the time is shown in Figs. 14, 15, 16 for the mixtures A, B and C.

The results obtained are typical of natural rubber that has been vulcanized by means of conventional sulphur vulcanization systems in the sense that the maximum crosslinkage density will decrease when the vulcanization temperature increases, as is apparent from Fig. 17.

The rate at which the number of effective crosslinkages decreases as a function of the vulcanization temperature over a larger temperature range (140°C–200°C) of a typical sulphur-vulcanized natural rubber mixture is also shown in Fig. 17. Data for this later curve has been taken from Gummi Asbest Kunststoffe 34, page 124, 1981, E.R. Rodger.

As is apparent from the figures the agreement between the times up to the start of the vulcanization which has been determined chemically (Figs. 14, 15 and 16) and the times up to the ε_r-minimum values determined dielectrically (Figs. 8, 9, 10 and 11, 12, 13) is very good.

In addition to correctly indicating the start of the vulcanization the dielectric method has also been found to give valuable information about the degree of vulcanization. In Fig. 18 the times up to t_{50}, i.e. the time necessary to reach 50% of full vulcanization measured chemically, on one hand—$t_{50\ chem}$ (min)—and by the rheometer—t_{50} rheometer—, on the other hand have been plotted as a function of t_{50} dielectric.

In general it can be observed that the Monsanto rheometer gives longer t_{50}-times than the isothermally determined $t_{50\ chem}$ and $t_{50\ diel}$ times. These results agree well with those previously indicated in so far as the Monsanto rheometer gives longer vulcanization times than measuring methods operating under isothermal conditions.

Example 2

The method of the invention is applied to a natural rubber mixture D with an EV-vulcanization system.

As previously mentioned and also apparent from the previous table the conventional sulphur/accelerator system in mixture A has been exchanged for an accelerator/sulphur donor system in mixture D.

In Fig. 19 dielectric curograms for mixture D are shown taken at 300 kHz and about 130, 140, 150 and 160°C. ε'_r as a function of the time shows the same initial course as for the mixtures A, B and C, i.e. ε'_r first decreases. As distinguished from the mixtures A, B and C the curogram of mixture D has two inflection points marked by whole arrows ($\varepsilon'_{r\ min}$) and dashed

arrows ($\varepsilon'_{r\,max}$) in Fig. 19.

In Fig. 20 $\Delta\varepsilon'_r$ is shown as a function of the vulcanization time. The inclination of the left sides of the loops and the maximum value of $\Delta\varepsilon_{r\,max}$ are increased when the vulcanization time is increased. The width of the loops increases when the vulcanization temperature is reduced.

In Fig. 21 the chemically determined crosslinkage density of mixture D is shown as a function of vulcanization temperature and time. The maximum crosslinkage density at different vulcanization temperatures varies much less than for the mixtures A, B and C which is in good agreement with previously known results.

In Fig. 22 $t\Delta\varepsilon_{r\,max\,diel}$ (marked by dashed arrows in Fig. 19) has been plotted as a function of $t_{50\,chem}$ (min) and $t_{50\,rheo}$ meter (min) in the same way as in Fig. 18.

It is apparent from Figs. 19 and 21 that the vulcanization start $\varepsilon'_{r\,min}$ (see also $\Delta\varepsilon'_r=0$ in Fig. 20) well coincides with the vulcanization start determined chemically (Fig. 21) while $\varepsilon'_{r\,max}$ is well correlated with $t_{50\,chem}$ (min) which has been plotted in Fig. 22 together with $t_{50\,rheometer}$ (min).

In the same way as for mixtures A, B and C the rheometer also gives longer vulcanization times for mixture D than for the isothermal methods.

Example 3

The method of the invention is applied to mixtures F, G, H and I of natural rubber with conventional sulphur/accelerator systems and with a varying amount of sulphur.

If a measuring technique is to be of any value for e.g. mixture development and/or routine testing of rubber mixtures the method should be able to detect not only big changes in the vulcanization characteristic exemplified by mixture A–D but also be able to detect *small* changes such as small variations in the sulphur content. In order to investigate the ability of the dielectric method to detect variations of rubber mixtures that might be designated as normal mixture to mixture variations which may arise under industrial conditions the mixtures shown in the following table 2 were investigated.

	F	*G*	*H*	*I*
SMR CV 60	100	=	=	=
ISAF N220	45	=	=	=
Dutrex 729 HP	8	=	=	=
ZnO	4	=	=	=
Stearic acid	1	=	=	=
TMQ	1.5	=	=	=
6 PPD	1.5	=	=	=
Microcrystalline wax	2	=	=	=
CBS	0.8	=	=	=
Sulphur	1.5	2.0	2.5	3.0

Concerning abbreviations, see table 1.

Dielectric curograms ($\Delta\varepsilon'_r$ as a function of the time) for the mixtures F–I recorded at 300 kHz and the temperatures 140 and 160°C are shown in Figs. 23 and 24.

$\Delta\varepsilon'_r$ as a function of the time has, as is expected, the same form as the curves previously reported in Fig. 11, i.e. $\Delta\varepsilon'_r$ increases the whole time monotonously for the curograms recorded at 140°C while $\Delta\varepsilon'_r$ of the curograms recorded at 160°C of the two lowermost sulphur contents (1.5 and 2.0 phr.S) reaches a constant $\Delta\varepsilon'_r$-value more quickly the lower the sulphur content is.

As is apparent from Figs. 23 and 24 $\Delta\varepsilon'_r$ is very sensitive to the amount of sulphur in the mixture—more sensitive the higher the vulcanization temperature is.

The following general conclusions can be drawn from the dielectric curograms shown in Figs. 23 and 24.

a/ An increased amount of sulphur and increased temperature will result in $\Delta\varepsilon'_r$ increasing faster than if the sulphur content and the temperature are low. This agrees well with what is previously known about the network structure of the sulphur vulcanized natural rubber in the sense that high sulphur contents in combination with high vulcanization temperature generate a polar network which is reflected here in the form of increasing capacitance.

b/ The start of vulcanization is detected quite correctly by means of the dielectric method as compared with the chemically determined crosslinkage densities of mixtures F and I shown in Fig. 25. When the sulphur content is reduced the start of the vulcanization is moved towards longer times which agrees well with the results obtained by means of the Monsanto Rheometer, however with the essential difference that the dielectric results, as a consequence of the completely isothermal conditions under which these are recorded, are displaced towards shorter times, which is apparent from the tables in Figs. 23 and 24.

c/ The $\Delta\varepsilon'_r$-curves reach constant values more quickly the lower the sulphur content is and the higher the temperature is, as is shown in Figs. 23 and 24.

Dielectric vulcametry, i.e. in-situ measurement of how the dielectric properties of vulcanizing

rubber are changed as a function of vulcanizing time and temperature has been found to give valuable information about the start of the vulcanization and the degree thereof. Dielectric vulcametry has turned out to be a powerful tool in mixture development because the method has a high sensitivity to minimal changes in the concentration of e.g. vulcanizing agent, accelerators and retardants.

Another advantage of the dielectric method as compared with previously known analysis techniques—mechanical rheometers—is that the amount of test material required per analysis is very small (less than 0.5 g) so that the analysis can be carried out under quite isothermal conditions because the test material can be heated to the predetermined temperature in less than one second.

Another advantage of the dielectric technique is that it makes possible the measurement of the course of vulcanization directly in the vulcanized products by using the multi-channel electrode described in Swedish patent application 8501270–6.

The invention is not restricted to what has been described above and shown in the drawings but can be changed and modified in several different manners within the scope of the invention defined in the claims.

CLAIMS

1. A method for determining basic values of a material specimen for analysis of its vulcanization characteristic, wherein the specimen is shaped under pressure and at a temperature preferably in excess of 100°C to a predetermined form and thickness between two electrodes (4) having plane-parallel sides facing each other which are brought into intimate contact with the shaped body during shaping in order to form a capacitor (13) whereafter the basic values being the capacitance (C) and loss angle (D) of this capacitor and the temperature of at least one of the electrodes (4), are measured and recorded simultaneously.

2. A method as claimed in claim 1, wherein the specimen is shaped in a cavity (12) having the requisite predetermined form and thickness provided in a specimen carrier (10) made from an electrically non-conductive material and having plane-parallel sides which is placed between the electrodes (4).

3. A method as claimed in claim 2, wherein the specimen carrier (10) is heated to the intended temperature before the specimen is placed in the cavity (12) thereof to be shaped.

4. A method as claimed in any one of the preceding claims, wherein the predetermined thickness is less than or equal to 1 mm and preferably less than or equal to 0.25mm.

5. A method as claimed in any one of the preceding claims, wherein the capacitance (C) and loss angle (D) are measured by means of an impedance analyzer (9) and the temperature of the electrode plates (4) by means of a thermoelement (6) connected to a digital thermometer (7) with an analog output.

6. A method as claimed in any one of the preceding claims wherein the basic values are determined at a temperature in the range of from 120 to 190°C.

7. A method as claimed in any one of the preceding claims wherein the basic values are determined at a frequency of at least 10kHz.

8. A method as claimed in claim 7 wherein the frequency is in the range of from 200 to 300 kHz.

9. An apparatus for the determination of basic values from a material specimen for analysis of its vulcanization characteristic, which comprises two electrodes (4) having plane parallel sides facing each other and which are adapted to be heated to temperatures preferably in excess of 100°C and adapted to compress a material specimen placed between them to a predetermined shape and thickness in order, by intimate contact with the body shaped from the specimen, to form together with the body a capacitor (13), a means (11) connected to the electrodes (4) for measuring the capacitance (C) and loss angle (D) of the capacitor and a temperature sensing menas (6, 7) connected at least to one electrode (4) for determining the temperature, the means for measuring the temperature, capacitance and loss angle being connected to a unit (8) adapted to record the resulting values as basic values.

10. Apparatus as claimed in claim 9, wherein the electrodes (4) are supported by plattens (2) included in a press (1).

11. Apparatus as claimed in claim 9 or claim 10, wherein the temperature sensing means comprises a thermoelement (6) and a digital thermometer (7) with an analog output, the thermoelement being connected to and galvanically separated from the electrode (4).

12. Apparatus as claimed in any one of claims 9 to 11, which further comprises a specimen carrier (10) of an electrically non-conductive material and having plane-parallel sides which is adapted to be located between the electrodes (4) and to enclose in a cavity (12) of requisite predetermined shape and thickness the material specimen during its shaping and vulcanization.

13. Apparatus as claimed in any one of claims 9 to 12, wherein the platens (2) of the press also are heat plates for heating the electrodes (4) and consequently the specimen carrier (10) and the material specimen to the intended temperature, the heat plates being connected to their

respective temperature regulators for adjusting the temperature.

14. Apparatus as claimed in any one of claims 9 to 13, wherein the unit recording the basic values is a 3-pen writer (8).

15. A method as claimed in claim 1 substantially as hereinbefore described with reference to the examples.

16. An apparatus as claimed in claim 9 substantially as hereinbefore described with reference to and as illustrated in Figs. 1, 2, 4, 5 and 7 of the accompanying drawings.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd, Dd 8991685, 1987.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.