

# ON THE CONDUCTIVITY OF CARBON COMPOUNDED RUBBER AND A NEW METHOD OF GRADING RUBBER COMPOSITIONS

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It is well known that since the discovery of carbon blacks as active and essential fillers of rubber compositions the electrical conductivity of rubber can be varied in a great range from a highly insulating material to a good conductor. There are some results already published about the conductivity of rubber compounds with various carbon blacks (see literature references at the end of the article). The curves given are however vague and the range of conductivity from 10 Megohm to 1 million Megohm has not been studied in detail so that it seemed to be worthwhile to investigate these rubber compounds and the mechanism of the carbon rubber conductivity more thoroughly.

## TEST SAMPLES

As the laboratory at first did not have the facilities of compounding rubber the mixing was done in an industrial laboratory. A master-batch as simple as possible should be mixed with such an amount of various carbon blacks that an extruded 7 mm. diam. stick 40 mm. long cured in a steel mould with inserted electrodes on both ends would give an electrical resistance between  $10 \times 10^6$  to  $10 \times 10^{12} \Omega$ . The cured samples should be hard and similar in appearance and size to the resistors used in electronics industry.

To make them hard a certain amount of sulphur had to be maintained in the master-batch.

The curing was done at first in a bipartite steel mould which was screwed together by 4 steel screws in the corners of the mould. The exerted pressure was so high that the soft uncured rubber filled completely the 4 cavities of the mould and flowed round the inserted electrodes. Some cavities in the mould were provided to take the overflow. The mould was then put into a thermostatically controlled oven which already was heated to the curing temperature. After curing, the 4 samples were taken out of the mould, allowed to cool down and the resistance of each sample was measured between the two electrodes inserted on both ends.

The electrodes consisted of tinned copper wire about 0.5 mm. thick, bent into a hook on one end. This hook was inserted into the mould and completely surrounded by the hard rubber mixture.

The results of the first half-year were completely discouraging. There was not any clear relation between the resistance and the carbon content, the composition of the mixture, the curing time or temperature. The resistance of the same rubber-batch cured several times at the same temperature

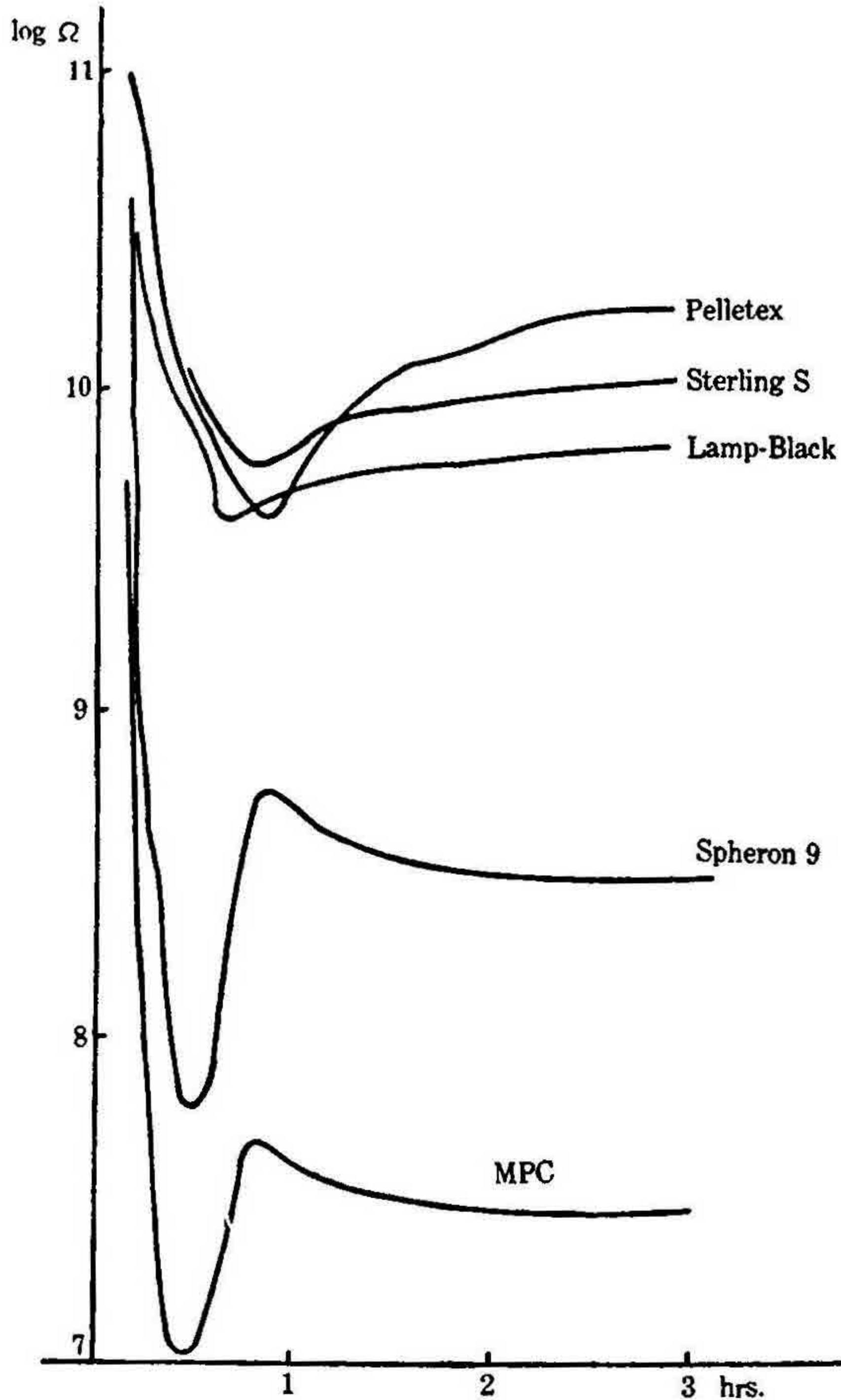


FIG. 1

in the same mould (four resistors could be made at a time) showed big variations. When the same composition was mixed in the industrial laboratory a second time quite different values were likely to be measured. The

quotation of a rubber chemist: "You cannot leave rubber alone, it is like that", was no comfort in our work.

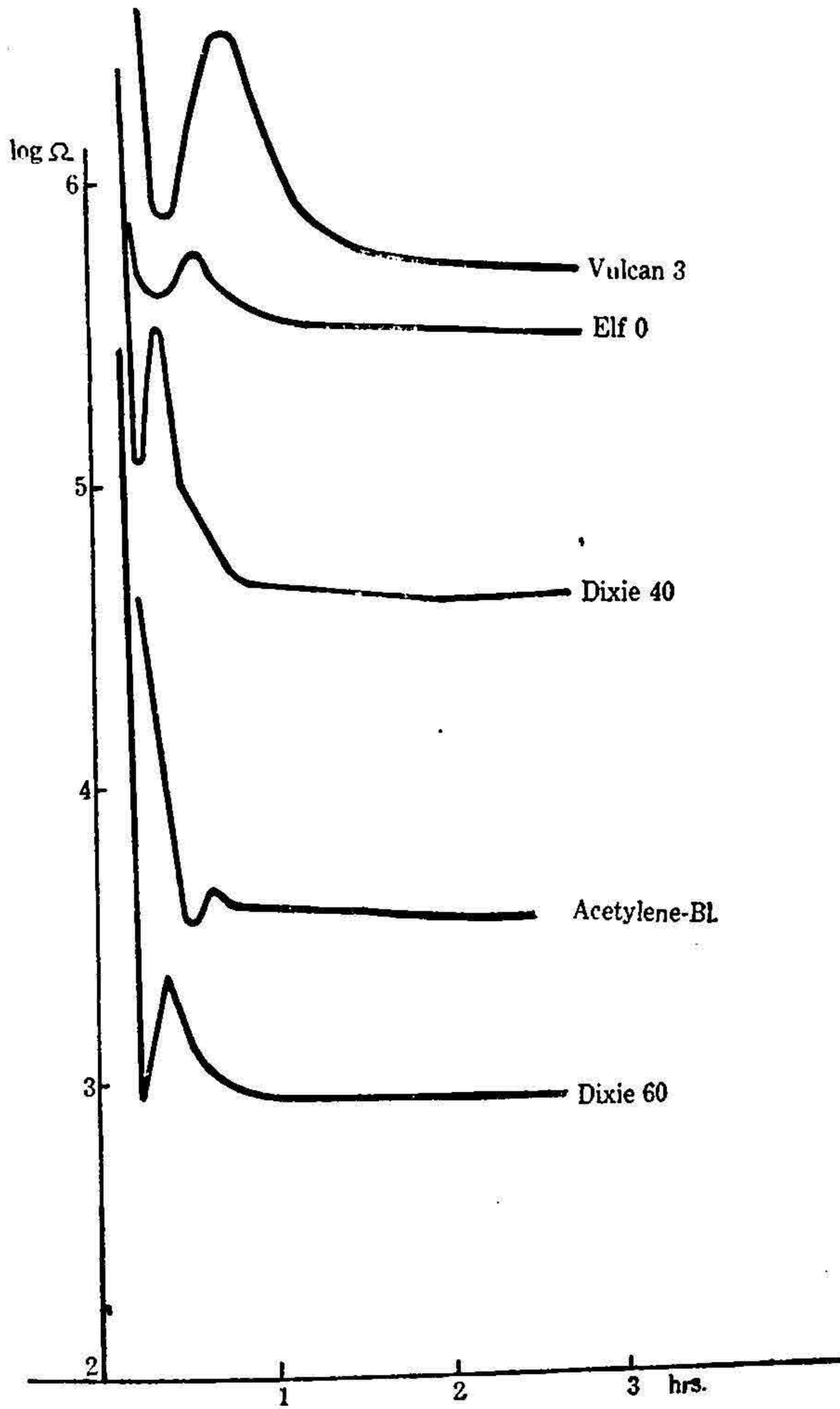


FIG. 2

The careful investigation of the samples so far used showed that the conductivity in most of the cases occurred only on the surface; grinding the surface with emery paper made all resistances infinite. The temperature

coefficient was positive and high, the voltage coefficient between 500 and 100 V was extremely high and variable.

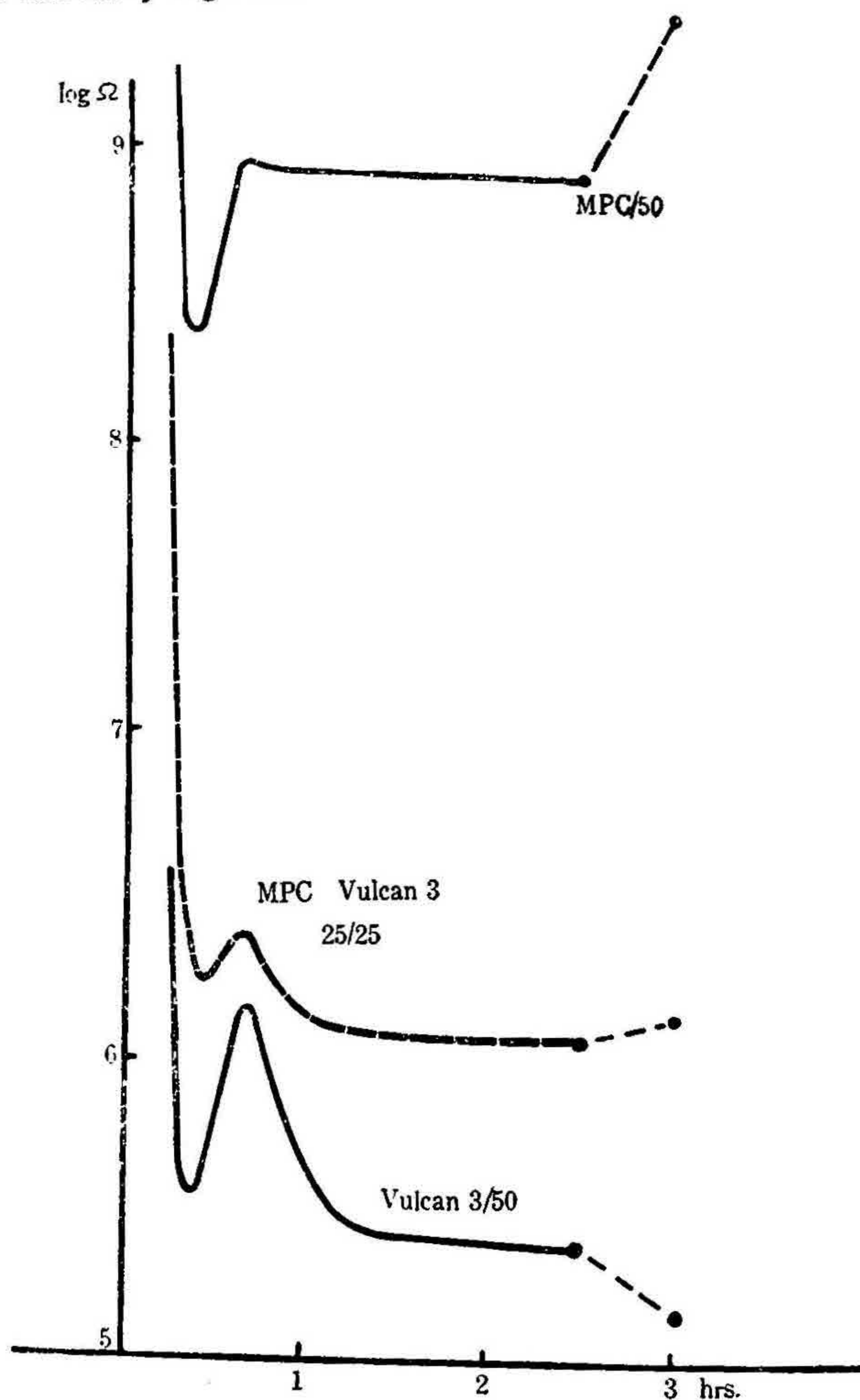


FIG. 3

As the resistance of the rubber composition in the uncured state was nearly infinite and after curing showed conductivity at least on the surface, it was decided to investigate the process of curing by recording the resistance during that time. The uncured extracted rubber sticks 40 mm. long were

split on both ends so that the electrode hooks could be inserted. The hooks were dipped before insertion in benzol. The small remnants of benzol on the hook were sufficient to wet the cut surface so that the rubber stuck when pressed together between thumb and forefinger. The soft stick was

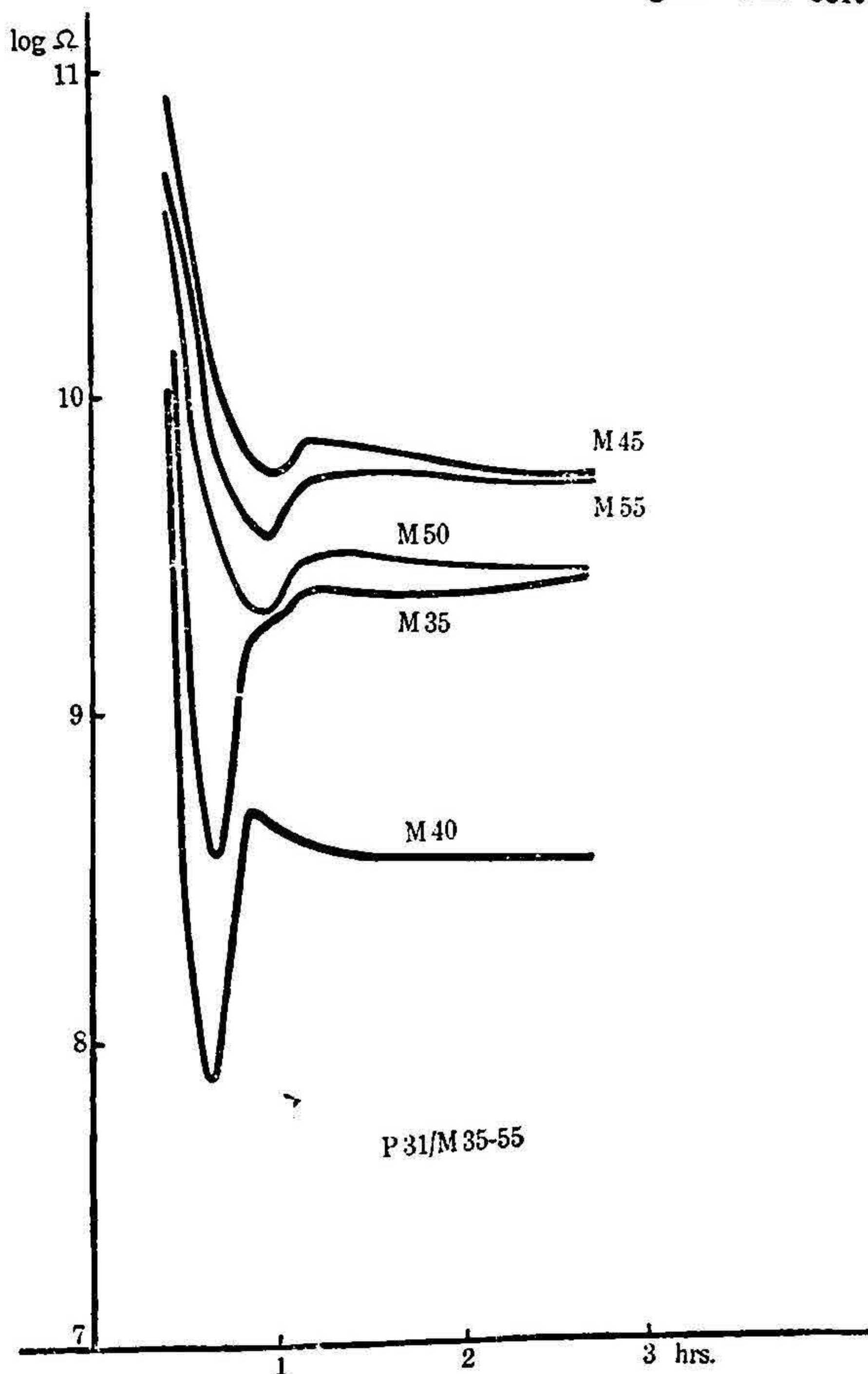


FIG. 4

then introduced into a glass tubing about 60 mm. long and 7 mm. diameter and put into the curing oven with the shielded measuring leads connected. The curves of the resistance *versus* time showed again all sorts of irregularities and no clue could be derived from these measurements. The expan-

sion of the samples also varied, some seemed to have been jammed by the glass wall and seemed to be cured under higher pressure than others.

Therefore some samples were prepared as similar as possible, rested on a glass plate so that they could expand freely in all directions except the small

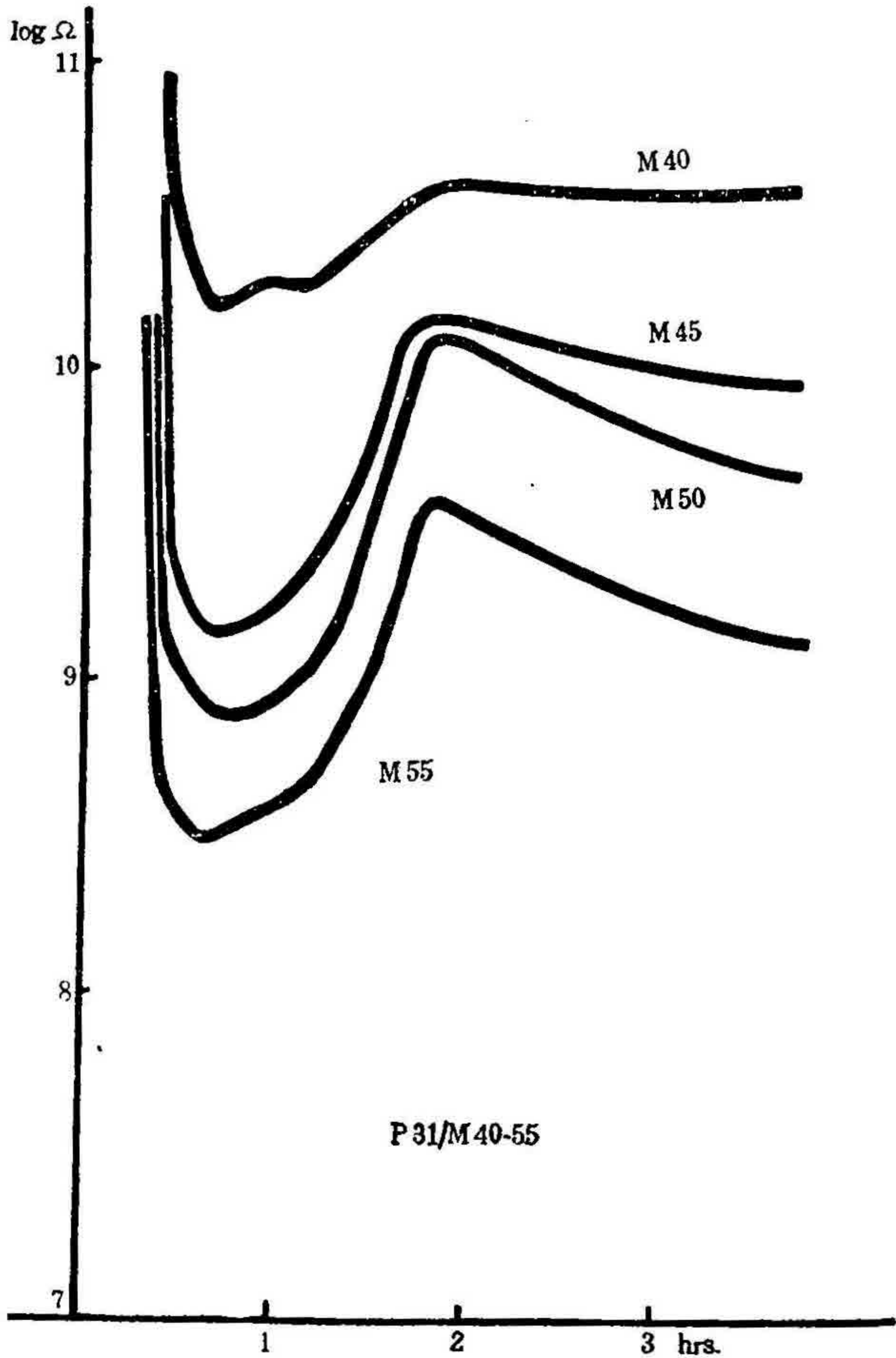


FIG. 5

part where the electrodes were inserted. These ends were bandaged to avoid any loosening of the electrodes. In this arrangement the measurements of the same compound gave for the first time the same and reproducible results and so this method provided the clue for further investigation.

In the new arrangement one electrode each of at least 10 samples could be screwed on to the terminals of 10 shielded cables. The cables used were high frequency flexible metal shielded cables about 3.6 mm. outside diameter. The insulation consisted of special grade porcelain beads. The shielded

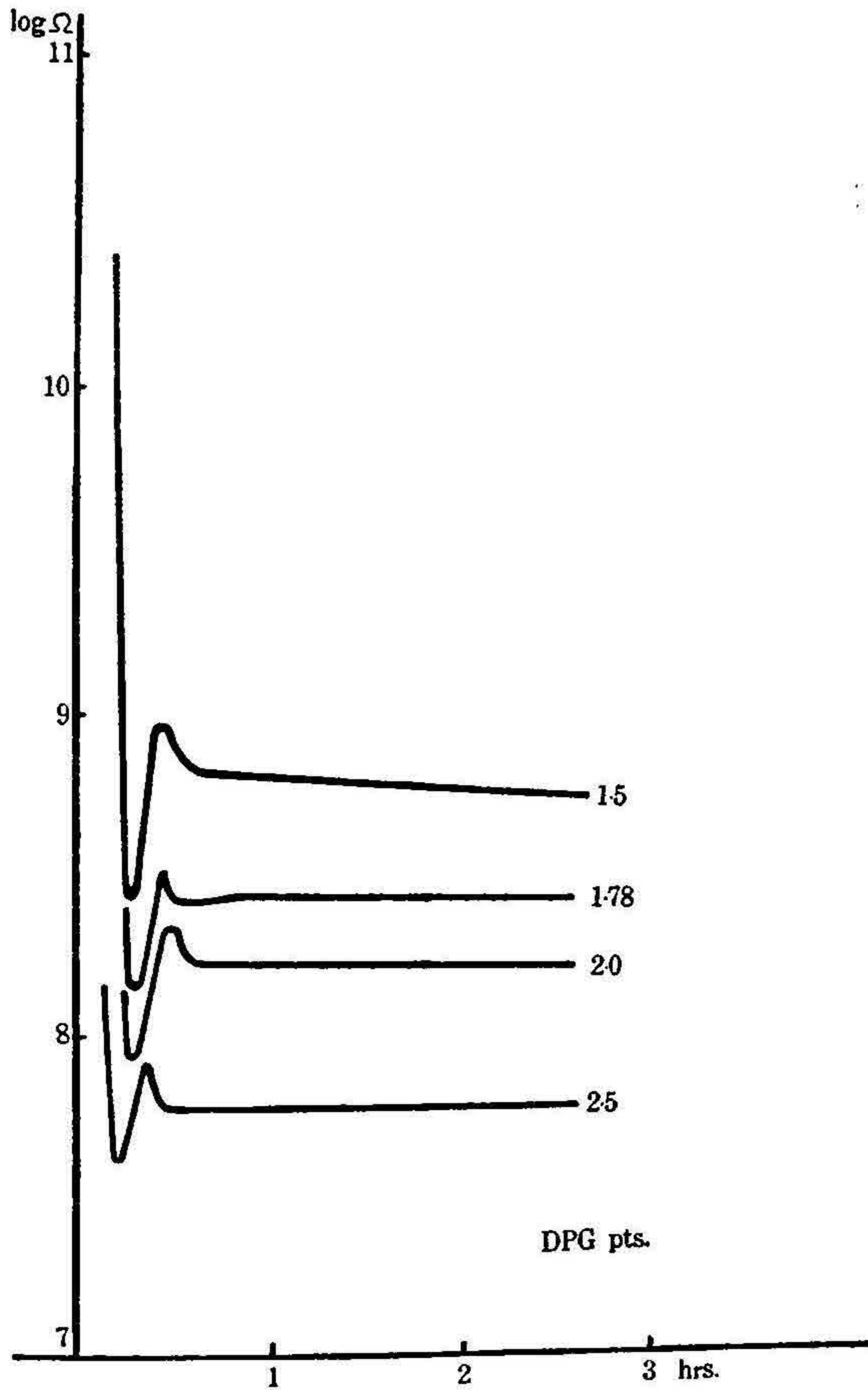


FIG. 6

terminals and the resistors were rested on a glass plate whereas the other ends of the resistors were connected with the tension lead. The measuring voltage was 500 V. D.C. Outside the oven a screened selector switch was

used to connect one of the resistor at a time to the measuring bridge. The instrument used was a General Radio Megohm bridge type 544 BA.

The samples were fixed to the shielded terminals and to the voltage lead in the already heated oven and the door was closed. Immediately after insertion one measurement was taken which showed for all resistors infinity. After 3 to 5 min. the insulation resistance started to decrease and then the measurements were taken every 2 to 5 min. according to the speed of change. In this way the various compounds were investigated.

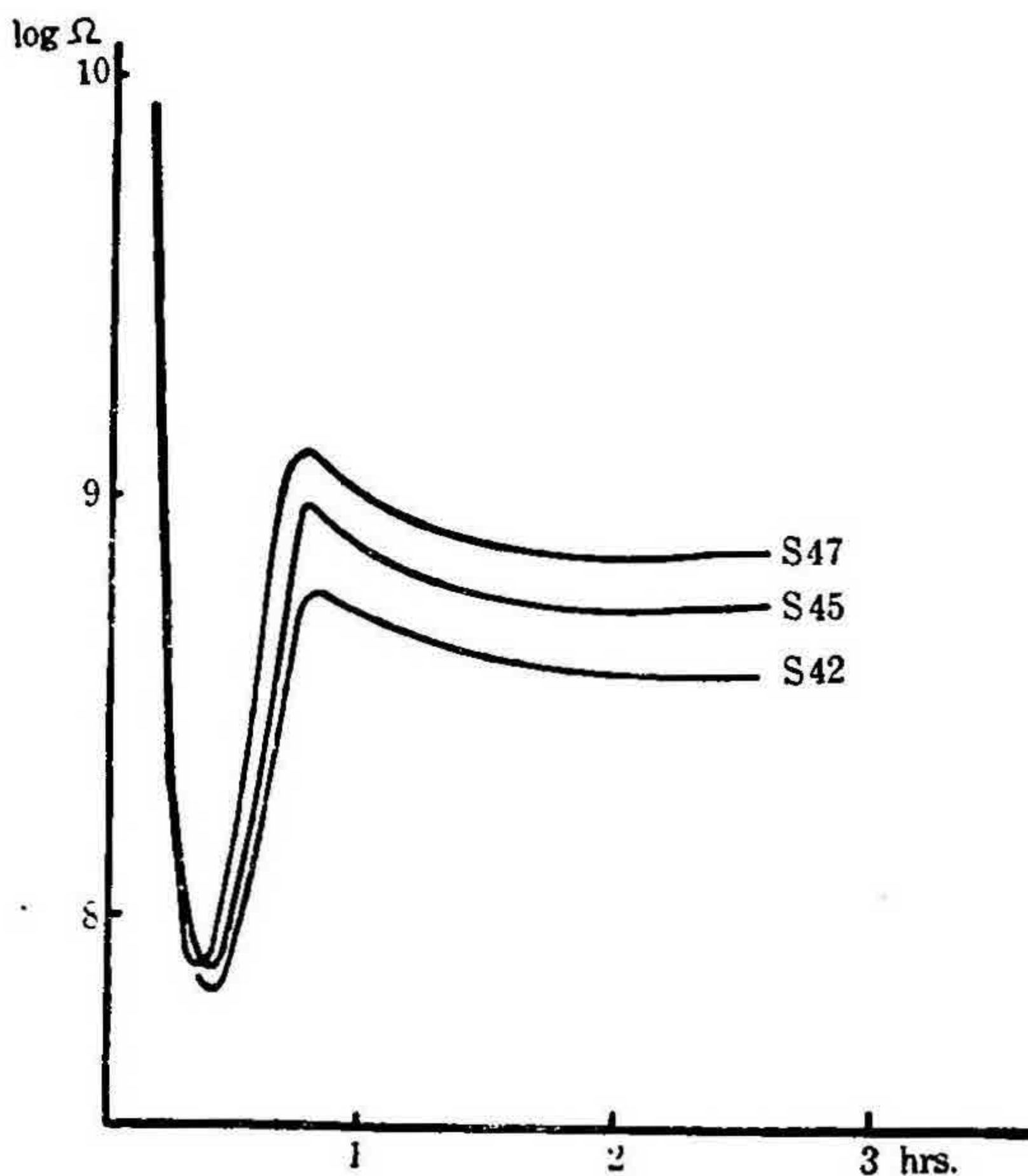


FIG. 7

One master-batch for the investigation of carbon blacks was made as follows:

Rubber	..	..	..	100
Carbon black	..	..	..	50
Sulphur	..	..	..	47
Mag. oxide	..	..	..	12.0
D.P.G.	..	..	..	1.75

The following carbon blacks 50 pts. in 100 pts. rubber were mixed into the M.B.: Pelletex S, Sterling S, Lamp Black, Spheron 9, M.P.C., Vulcan 3



Elf 0, Dixie 40, Acetylene Black, Dixie 60. The results are given in Figs. 1 and 2 (see pages 40 and 41).

As all these curves could be reproduced within at least 10% of the end value, no better view of the effect of the various carbon blacks can be given than by those curves.

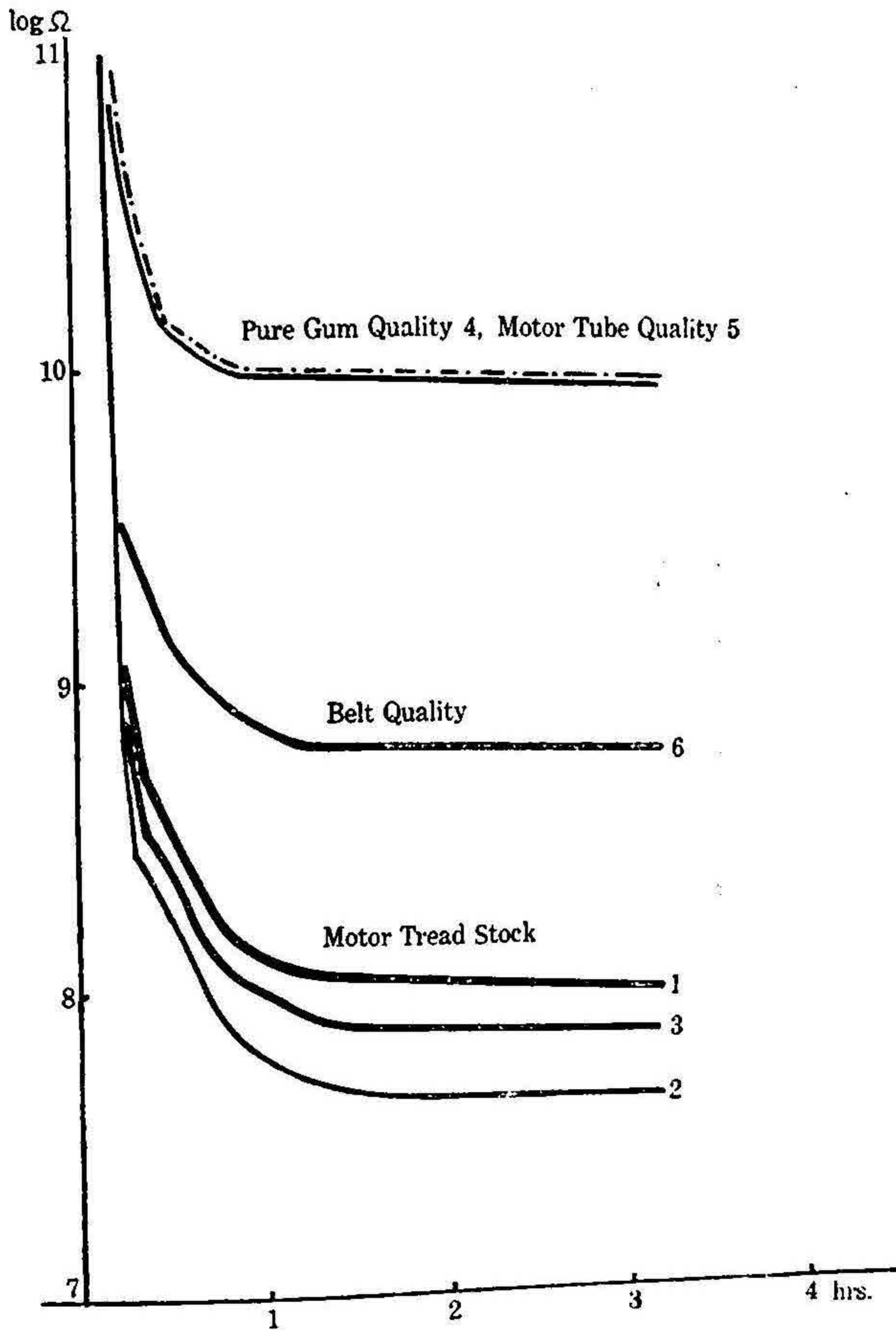


FIG. 8

Moreover at the end of each series of measurements the temperature coefficient of each compound was determined. Some of the mixtures show a positive temperature coefficient as e.g., M.P.C., some a negative temperature

coefficient as *e.g.*, Vulcan 3; Fig. 3 (see page 42). This was a very new and striking observation. It shows that the molecular bonding and the size of the carbon blacks play an important role. Similar observations have been made with metals in thin layers. As soon as the thickness of the metal film decreases below a certain value the temperature coefficient changes from positive to negative values.

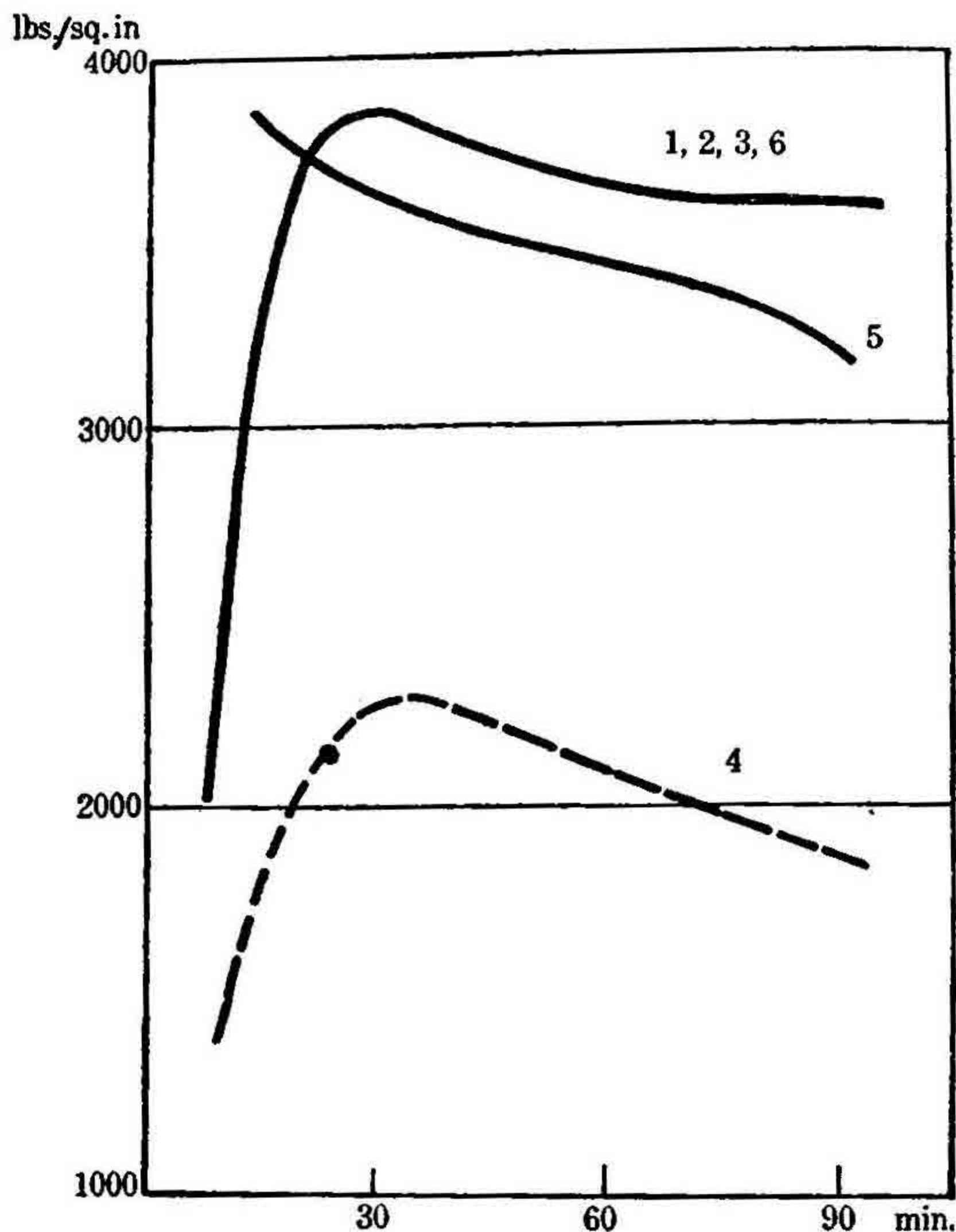


FIG. 9

By mixing two carbon blacks with positive and negative temperature coefficients the resultant compound shows only a very low temperature coefficient (Fig. 3). This result is of very great importance for the production of carbon resistors with practically no temperature coefficient.

With another M.B., the influence of the various contents of carbon black M.P.C. (35 to 55 in 100 rubber) was studied. By means of the new method one is in a position to check very accurately and quickly the composition. Fig. 4 (see page 43) shows such a batch with varying carbon blacks M.P.C. where the composition has been really "mixed" up. The application

of the new test method indicated at once that something must have gone wrong during the mixing. The industrial laboratory was asked to prepare a new master-batch with samples of varying carbon content from 35 to 55 pts. in 100 rubber with more care and the results then turned out according to the theory (see Fig. 5, page 44).

In the same way, the influence of D.P.G. and of sulphur content was tested. Fig. 6 (see page 45) shows the influence of various parts of D.P.G. Fig. 7 (see page 46) shows the effect of various parts of sulphur in a similar M.B.

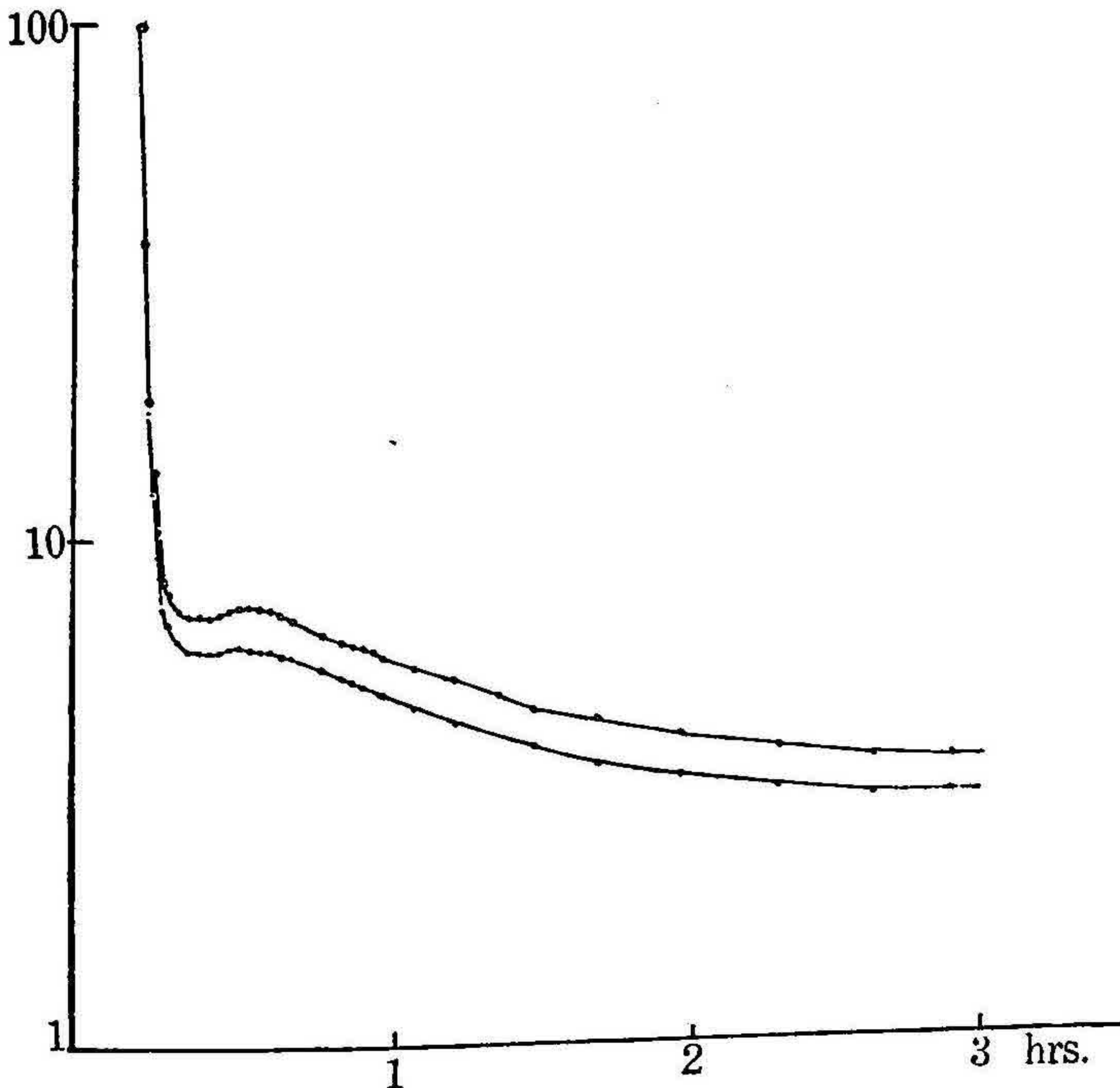


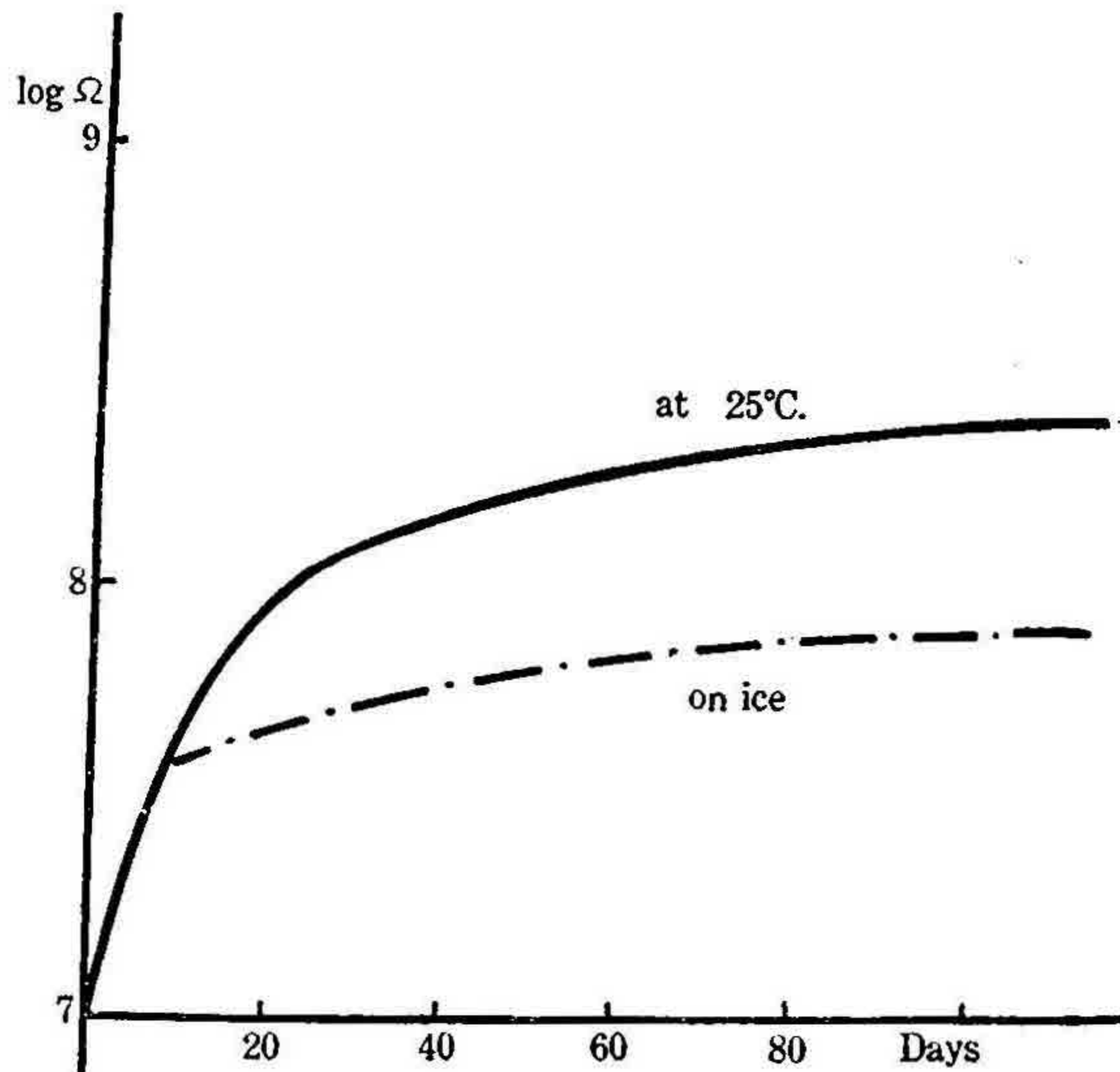
FIG. 10

It was of interest to apply the new method also on the standard soft rubber qualities used in the Tyre- and Tube-industry. The results are shown in Fig. 8 (see page 47). Fig. 9 (see page 48) shows for the same rubber batches 1 to 6 the tensile strengths *versus* curing time in minutes.

The following soft rubber composition was milled and cured at 135° C. and the result is shown in Fig. 10.

Rubber .. ..	100
Stearic acid .. ..	3.00
Pine tar .. ..	3.00
Agerite powder .. ..	1.00
M.P.C. .. ..	47.50
Zinc oxide .. ..	3.00
Sulphur .. ..	3.00
M.P.T. .. ..	1.00
	161.50

There is no obvious relation between the resistance curve of the sample and the curing rate at which the soft rubber mixtures possess maximum tensile



P32/M50 S45

FIG. 11

strength or maximum elongation. However, the electric resistance curves during vulcanisation are so characteristic for each batch that they should be made a supervisory element in the tyre factory for each new mixture. Any small deviation or any slip of the mixer will be shown at once in the curve. To test a rubber batch by the electrical method is not only more accurate but

it is quicker. Upto now a rubber manufacturer has to cure at least one big sheet of every new compound from which samples have to be tested for tensile strength and elongation after a curing time of 5, 10, 15, 20 and so on upto 50 minutes. Although the variation of the mechanical properties

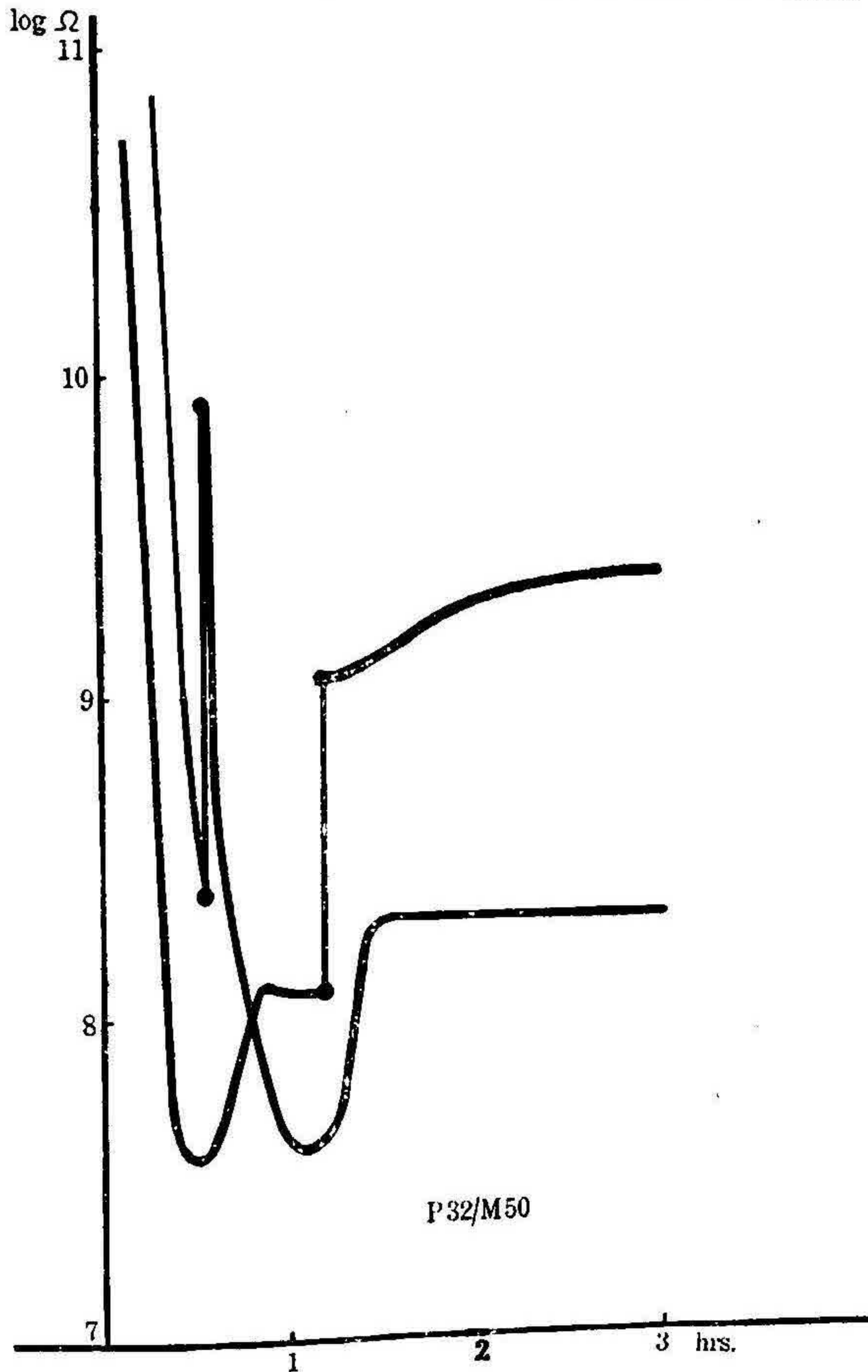


FIG. 12

of a batch of 20 samples cured for a certain time is rather large the averages of these values are nevertheless used to draw a curve as shown in Fig. 9.

With the new method, 4 different batches can be easily tested in one run of two hours by one laboratory helper so that one batch requires only 30

minutes respectively to draw the complete resistance curve *versus* temperature.

The ageing of uncured rubber compositions with D.P.G. has been checked. Fig. 11 (see page 50) shows the resistance of a batch at the end of 3 hours curing time, containing D.P.G. 1.75, sulphur 45 in 100 pts. rubber at various intervals upto 3 months. After 10 days the batch was divided into two sections, one was stored in a refrigerator at about  $+4^{\circ}\text{C}$ .

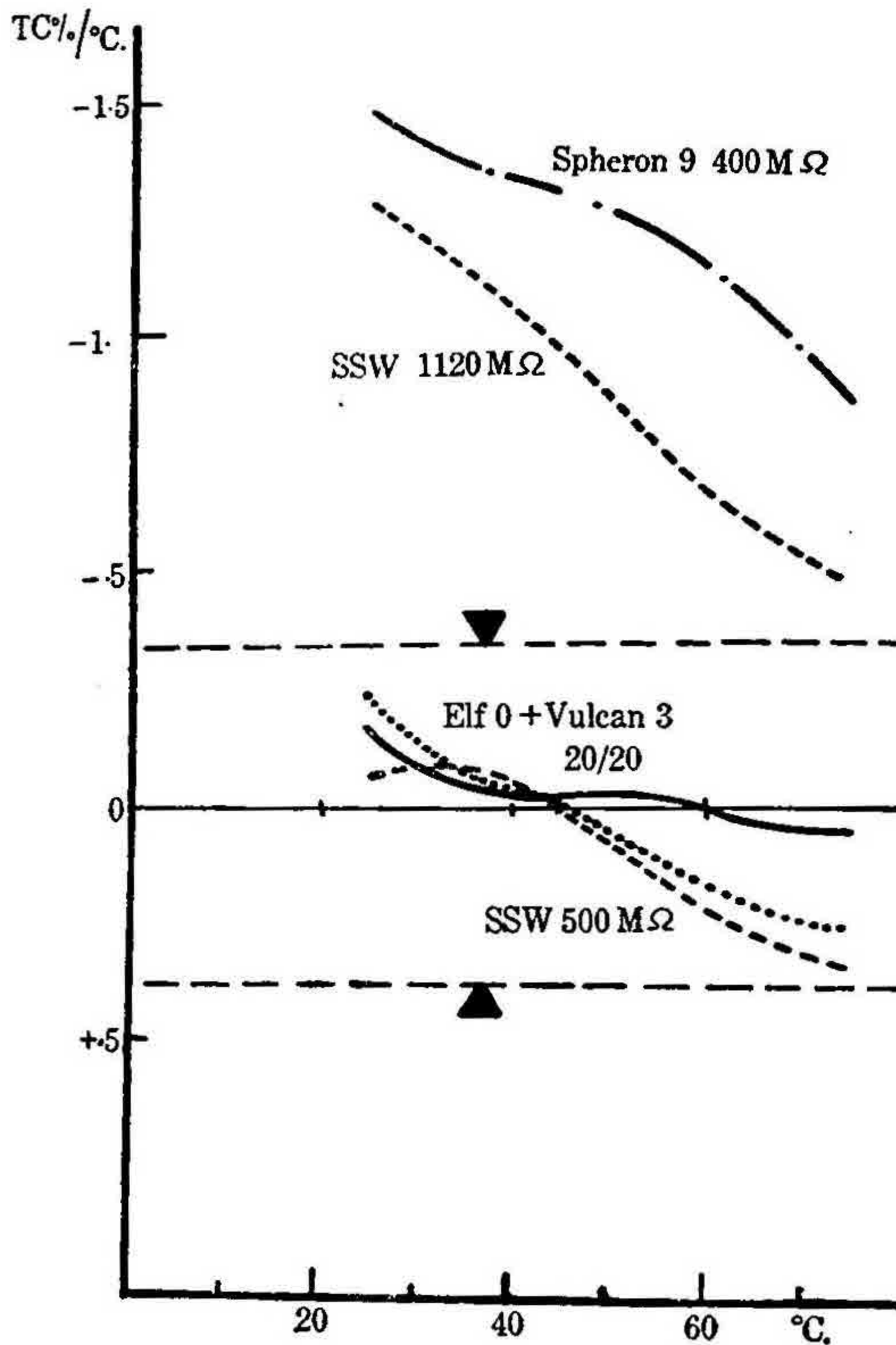


FIG. 14

the other remained at room temperature  $25^{\circ}\text{C}$ . The resistance of the batch stored at room temperature rises according to a log-function whereas cool storage acts as an inhibitor.

The new method proved to be a proper tool for checking and grading rubber compositions and for our further studies. To understand the characteristic curve of the resistance during the vulcanisation of the rubber-sulphur-carbon compound the process of curing of rubber has to be looked

on as a process of molecular kinetics and molecular equilibrium. In the first instance heating up the molecules increases the kinetic energy through the movements of molecules. This causes an electric contact between the various carbon molecules and an even distribution of the carbon molecules within the rubber molecules due to the absorption forces between the two different molecules. When the temperature further increases and the energy of activation for sulphur and D.P.G. has been reached, the double bonds in the rubber molecules break up, new carbons enter the rubber molecules and addition of sulphur to the rubber molecule takes place. The angle between carbon-carbon links in rubber molecules is  $108^\circ$ . Each single bonded carbon atom is free to rotate and contribute to the electrical resistivity. Shortly after that the 3-dimensional bonding between the long chains

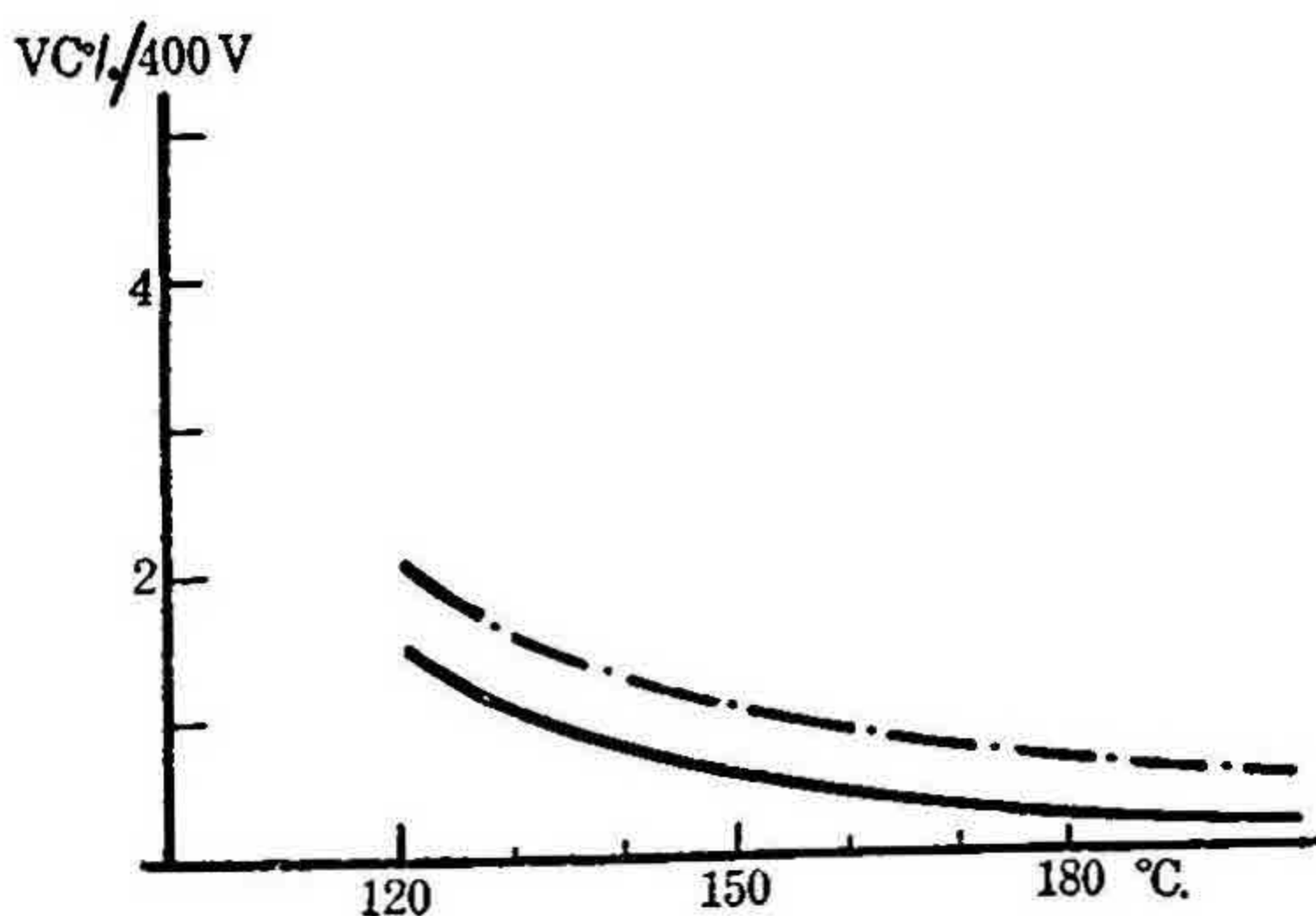


FIG. 15

of high polymer molecules takes place and brings the resistance to its ultimate value. This new conception of the happenings during the curing of rubber is based on the chemical reaction in a solid phase combined with a molecular absorption which is a component mechanism of a catalytic process. Each process can be expressed by the function  $p = Ae^{Bt}$ . The three processes can be visualised by the electrical method of measuring the resistivity during the curing time, provided the free movement and establishment of carbon-carbon links is not hindered.

With this conception, we are now able to understand our first discouraging results. The curing of rubber samples in glass tubes prevented the free movement of the molecule and the bonding of carbon was disturbed. A higher resistivity is the result. The value is unpredictable because the expansion of the rubber compound during curing can take place only in the longitudinal direction and by the friction between the surface of rubber

molecules and the glass wall a jamming effect can take place at any time giving erratic configuration.

If the new conception would be true, then any disturbance of the free movement at any time must increase the resistance. This has been shown in many experiments. One sample is given in Fig. 12 (see page 51) where pressure has been applied after 2 different times of curing. For this purpose the samples were cured in a porcelain mould. The results in the graph show the immediate increase of resistance with the application of pressure to the specimen.

### HIGH OHMIC VALUE RESISTORS

The understanding of the curing of rubber makes it possible to produce electrical resistors of the order of 10 megohms to 1 million megohms.

The demand for resistors of this order is very great and steadily increasing. Four main principles have been applied for the production of resistors of that order: (1) Low conductivity of liquid mediums, *e.g.*, Mannit Boracid acid composition in the following strength: 121 g/1 Mannit, 41 g/1 Boracid Acid, 0.06 g/1 KCl or Toluol-Alcohol-Picric Acid *et alias*. (2) Low conductivity of ionised air, *e.g.*, in ionisation chambers. (3) Thin metallic film, electrode sputtered or vapourised. (4) Carbon compound resistors.

According to the investigation carbon compound resistors on rubber base are very promising.

However, to realise the amount of investigational work which has to be done to achieve the really best solution one has to consider the following scope: A rubber compound normally consists of approximately 7 components besides the already mentioned ones, *viz.*, Rubber, Sulphur, Carbon. They may be listed as an example as follows: Accelerator, Antioxidants, Barites, Stearic Acid, Magnesium oxide, Zinc oxides, Barium carbonates.

At least 3 samples of the same mixture have to be made at a time, 3 each should have been cured at 4 various temperatures under different pressures and 3 various curing times.

At least 20 different carbon blacks are on the market which differ greatly in respect to molecular size, reaction with rubber, etc. The carbon content of each mixture should be varied at least 5 times, in the same way the content of sulphur should be varied at least 4 times. The 7 other components listed above would give as sum of the combinations at the various classes  ${}^7C_1 + {}^7C_2 + {}^7C_3 + {}^7C_4 + \dots + {}^7C_7$  the figure 127.

The total amounts then to 5,486 millions of resistor samples which should be made and tested, to give an answer to all our questions. If there



were only one combination which would be the perfect one then it would be nearly impossible for us to find the correct solution. However, with the new method of testing, a good deal of combinations may be discarded.

Samples of resistors which have been made so far in a split-cavity compression mould (see Fig. 13) show already a clear superiority against similar resistors which are available on the market in the following lines:

1. The temperature coefficient of the new resistors are lower. Some carbon mixtures have been found with extremely small temperature coefficient as can be seen from Fig. 14 (see page 52). In the same figure some values are given of carbon resistors which were bought on the market.

2. The voltage coefficient is smaller. In Fig. 15 (see page 53) the voltage coefficient *versus* temperature between 100 and 500 V. D.C. is shown for the new resistor type. Here again the superiority of the resistor manufactured according to scientific principles shows superiority against samples bought from the market.

3. The new resistors are practically free from Johnson noise and behave like wire-wound resistors. The Johnson noise was measured as the voltage produced in the resistor at room temperature 20–30° C. according to the formula

$$E^2 = 5.50 \times 10^{-23} TR\Delta f,$$

where  $E$  = noise voltage (r.m.s.)

$T$  = abs. temperature

$R$  = value of resistance in Ohm

$\Delta f$  = band width of measuring instrument in cps.

The measurements were taken by Mullards noise meter detector. Contrary to carbon resistors from the market the new types were noise-free at values upto several thousand megohms.

The progress is so striking that this research work will be continued.

The research work was started in the Defence Research Laboratories, Melbourne, Australia, and has been continued in the Indian Institute of Science. I wish to express my thanks to the Chief Superintendent of the Defence Research Laboratories, Mr. A. E. Dawkins, and to the Director of the Indian Institute of Science, Professor M. S. Thacker.

## LITERATURE REFERENCES

From the huge amount only a few literature references are given below.

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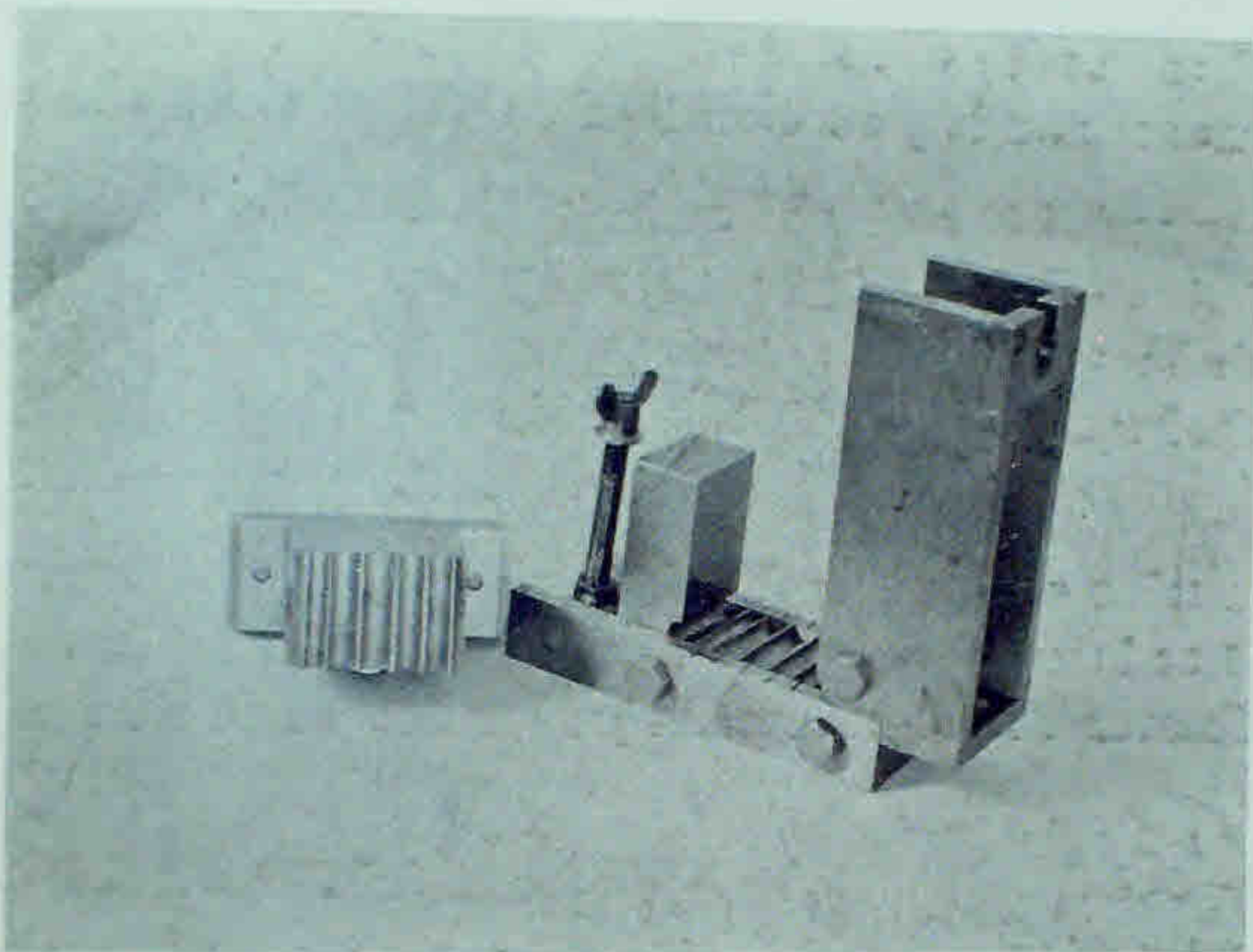


FIG. 13. Split cavity compression mould.