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PROPOSAL FOR A STUDY PROGRAMME OF THE EFFECT OF NUCLEAR RADIATION
ON ORGANIC INSULATING MATERIALS

by

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1. Introduction

The ionizing effects of radiation in organic insulators lead to a series of complex chemical reactions (predominantly cross-linkage or chain cleavage) which drastically alter the nature of the materials^{*)}.

Problems of radiation damage have been observed in the existing high-energy accelerators⁽¹⁾.

Possible improvements of the PS intensity will generate still more severe problems of radiation damage.

At present there are only limited data available which correlate laboratory tests and service life of a polymeric material at different radiation doses. However, on the basis of the rate of change of the polymer properties on exposure to radiation, it is possible to estimate life expectancy to some degree.

The property of radiation resistance of materials is becoming a factor that has to be taken into account in accelerator construction like other properties that one is used to work with. It is an unfortunate coincidence that those parts that are among the most delicate in accelerator engineering, namely the insulating materials, are also most subject to deterioration under the influence of radiation. At the present stage of knowledge it would be unwise to ignore these phenomena and it has therefore been

^{*)} A separate paper on this subject is being prepared.

decided to establish a research programme consisting of:

- 1) calculation of the life expectancy of existing important PS components, e.g. excitation and pole face windings. (Some work has been done already⁽²⁾);
- 2) determination of the distribution of the radiation dose in the tunnel during operation;
- 3) research into new radiation resistant materials with a view to construction of new PS parts, ISR and 300 GeV machine;
- 4) investigation of materials proposed by prospective constructors;
- 5) study of dose rate and LET (linear energy transfer) effects.

2. Study Programme - Tests

The failure of electrical insulations in nuclear radiation environments is primarily due to the mechanical and physical deterioration of the materials rather than the gross changes in their dielectric properties⁽³⁾.

The test programme can be divided into the following categories:

- a) mechanical changes: - flexural strength
 - hardness
 - bond strength
- b) physical changes: - heat distortion
 - viscosity
 - moisture absorption
- c) electrical changes: - dielectric strength.

The samples are in the form of machined or cast pieces, with dimensions $90 \times 20 \times 6 \text{ mm}^3$, requiring breaking loads of the order of 80 kg.

The mechanical tests consisted of a bending test performed on an instrument constructed in the Cern workshop. It allows in a simple way the determination of modulus of elasticity and flexural strength by the simultaneous measurement of applied force and sagitta. When measuring mechanical properties of polymers bending tests are to be preferred over tensile tests, as the latter present the difficulty of gripping the sample in a satisfactory way without the risk of slipping.

The radiations will be performed in the well-known field of a nuclear reactor, because high levels of irradiation can be obtained in a relatively short time.

To check our experimental techniques and to get familiar with the problems connected with this field of research a few test irradiations were carried out on polymers whose behaviour is known from other sources⁽⁴⁾, so that a direct comparison could be made. These irradiations can at the same time serve as references for point 4) of Chapter I.

Irradiations have been carried out in the Astra-Reactor, Seibersdorf, operated by the Austrian Atomic Energy Commission. This reactor is of the swimming pool type, with a maximum output power of 5 MW. This type of reactor is very convenient for irradiation studies due to the ease with which samples can be introduced and removed during operation and the simple provision of cooling facilities. Samples were introduced by means of an aluminium container which can take 18 samples at the time. The container, which was closed, was equipped with connections for air cooling and could easily be lowered in one of the holes in the graphite reflector. In this position the dose rate was approx. 10^8 rads/hour.

Already at this rate efficient cooling is necessary, as can easily be shown. A rate of 10^8 rads/hour corresponds to an energy absorption of about 0.3 W/g. In our samples this means that about 150 mW have to be eliminated per cm^2 of surface. The heat transfer coefficient for stagnant air can be taken as $1 \text{ mW/cm}^2 \text{ }^\circ\text{C}$, which shows that without cooling a surface temperature of 150°C would be reached. For resins a coefficient of thermal conductivity of about $5 \text{ mW/cm }^\circ\text{C}$ can be assumed. Thus an additional $\Delta T = \frac{150 \times 0.3}{5} \sim 10^\circ\text{C}$ will exist between the inside and the outer surface of the sample.

If no adequate cooling is provided, it will thus be impossible to distinguish between the damage introduced by temperature effects and by ionization.

However, for moderate air velocities the heat transfer coefficient increases rapidly, so that for most experiments, if closed packing of the samples is avoided, air cooling will be sufficient.

Water cooling is possible by putting the samples in a container and fill this with the pool water (40°C). This is a simple and efficient method.

The unit of radiation generally used where plastics are concerned is the "rad". One rad is equivalent to the absorption of 100 ergs. of energy per gram of material.

Another unit is the "Roentgen", being defined as that quantity of radiation which produces 1 e.s.u. in 1 cm³ of air at 0°C and 760 mm Hg. This is equivalent to the absorption of 83,8 erg. of energy from radiation by 1 g of air. It is clear that the rad is a much more convenient unit.

3. Materials to be studied

Among the plastics, the rigid types are the more radiation resistant materials. At present, the materials which will operate satisfactorily in the range of 10⁸ to 10⁹ rads are glass fibre- and asbestos-filled phenolics, certain epoxy systems, polystyrene, mineral filled polyester, mineral filled silicones, and polyvinylcarbazole. The most commonly used organic materials to insulate coils are: epoxy, polyester and silicone resins⁽³⁾⁽⁵⁾⁽⁶⁾.

It has been proved that some glass fibre reinforced and mineral filled epoxies show still higher radiation resistance⁽⁷⁾.

The curing system used has a large effect on the radiation stability of epoxy resins. Comparison of epoxy resins cured with different reagents showed that aromatic amines, acid anhydrides and catalytic curing agents give products that are much more resistant to radiation than those with aliphatic curing agents⁽⁸⁾.

The difference between the amine derivatives and the anhydrides lies in the fact that due to the great reactivity of the amine groups, the combinations based on these hardeners have a short potlife when heated to the temperature corresponding to a low viscosity. These systems are therefore used in the preimpregnated tapes ("prepregs") which are stored at low temperatures, wound on the conductor and only then heated to polymerizing temperature.

The standard impregnating resins used in the electrotechnical industry are all based on acid anhydride hardeners as only these combine low viscosity with long potlife.

On the basis of a theoretical study which will be reported in a future paper, and after discussions with chemists both from Ciba and Shell Chemical Company, the following systems have been retained for further study.

A. Resins suitable for impregnation

Conventional epoxy resins cured with acid anhydride and catalytic curing agents.

Epoxy novolak resins cured with acid anhydride curing agents.

(See Appendix).

B. Resins suitable for preimpregnated tapes

Conventional epoxy resins cured with aromatic amines as curing agents.

Epoxy novolak resins cured with aromatic amines.

C. Resins suitable for casting

Conventional epoxy resins cured with aromatic amines and acid anhydrides and filled with inorganic materials (fillers).

4. Results of preliminary tests (Figures 1, 2)

Samples prepared from epoxy resins cured with diamino diphenyl methane (DDM), phthalic anhydride and nadic methyl anhydride^{*)} have been irradiated. The latter showed a large spread in mechanical strength already before irradiation. The results after irradiation are therefore not given as they do not permit any valid conclusion to be drawn. The reason for this failure is that no prior experience with this hardener existed, resulting probably in insufficient mixing of the system and thus a large spread in properties. These tests will be repeated.

*) These hardeners are sold by Ciba.

Systems cured with DDM and phthalic anhydride retain about 50% of their mechanical strength at absorbed doses of about $3 \cdot 10^9$ rads. The samples darkened already after low levels of exposure (10^7 rads) but this shows no influence on mechanical properties. Above $4 \cdot 10^9$ rads the samples became too brittle for measurements. These results confirm those found by other researchers⁽⁴⁾.

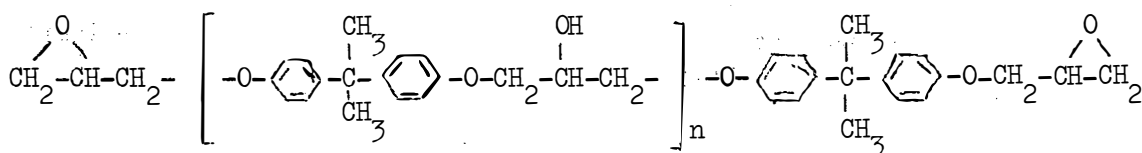
The low mechanical strength showed by the DDM hardener at about $2 \cdot 10^9$ rads is due to an accidental interruption of the flow of cooling air for half an hour. The samples immediately showed evidence of gas evolution, resulting in a high brittleness. These tests were repeated and extended to still higher doses, using water cooling.

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APPENDIX

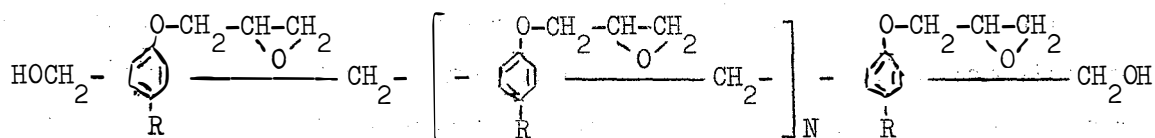
The well-known epoxy resins (conventional epoxy resins^{*}) are prepared by the reaction of a diphenol, such as diphenol propane, in the form of the alkali metal salt, with epichlorohydrin, to form a straightchain polymer, i.e.



Since in general these resin molecules contain only the two terminal epoxide groups, the resins will be called diepoxides.

The polyepoxide resins contain more than two epoxide $\left(\begin{array}{c} \text{---} \text{C} \text{---} \text{C} \text{---} \\ | \quad | \\ \text{O} \quad \text{O} \end{array} \right)$ groups per molecule, and this results in their having different properties and reactivities from those of the diepoxide resins.

The polyepoxide resins are derived from phenol-formaldehyde (or urea-formaldehyde or melamine formaldehyde) condensation products of novolak structure and epichlorohydrine. Interactions of the alkalimetal salts of these materials with epichlorohydrin yields epoxide resins with a plurality of epoxide groups depending upon the molecular weight of the novolak employed, e.g.,



Considerable variation in the products may be obtained by the use of different ratios of phenol to formaldehyde giving various chain-lengths, and by the use of substituted phenols.

* Araldite (Ciba), or Epikote (Shell)

The structure of these polyepoxide resins as compared with the diepoxide resins shows the following significant features:

- 1) Since no epoxide groups formed on the resin molecule are used up in chain-extension reactions, the polyepoxide resins contain a sufficient number of epoxide groups to enable some of them to be modified by suitable reagents while still leaving a sufficient number intact to act as cross-linking centres. In contrast, the diepoxide resins contain only the minimum number of epoxide groups necessary for cross-linking to occur.
- 2) The epoxide groups in the polyepoxide resins are closely packed and thus, on curing, more rigidly cross-linked structures are formed than can be obtained with the diepoxide resins.

Curing may be established using materials classed as hardeners or curing agents. These react to polymerize epoxy resins through either one of the two methods:

- a) catalytic means in which the epoxide groups on the resin molecules interact (example: boron trifluoride complex) or
- b) by cross linking, in which copolymerizing molecules unite with the epoxyresin molecules becoming part of the cured resin network (examples: aromatic amine and acid anhydride curing agents).

In both cases, the epoxide groups are opened, and subsequently a closely knit polymer structure is formed.

The resin manufacturers usually incorporate into epoxy resins diluents or modifiers which will selectively alter properties to suit specific requirements, e.g. low viscosity, better adhesion and mechanical strength. Actually any liquid aromatic hydrocarbon that contains an epoxide group and has lower viscosity than the resin could be used as a diluent.

References:

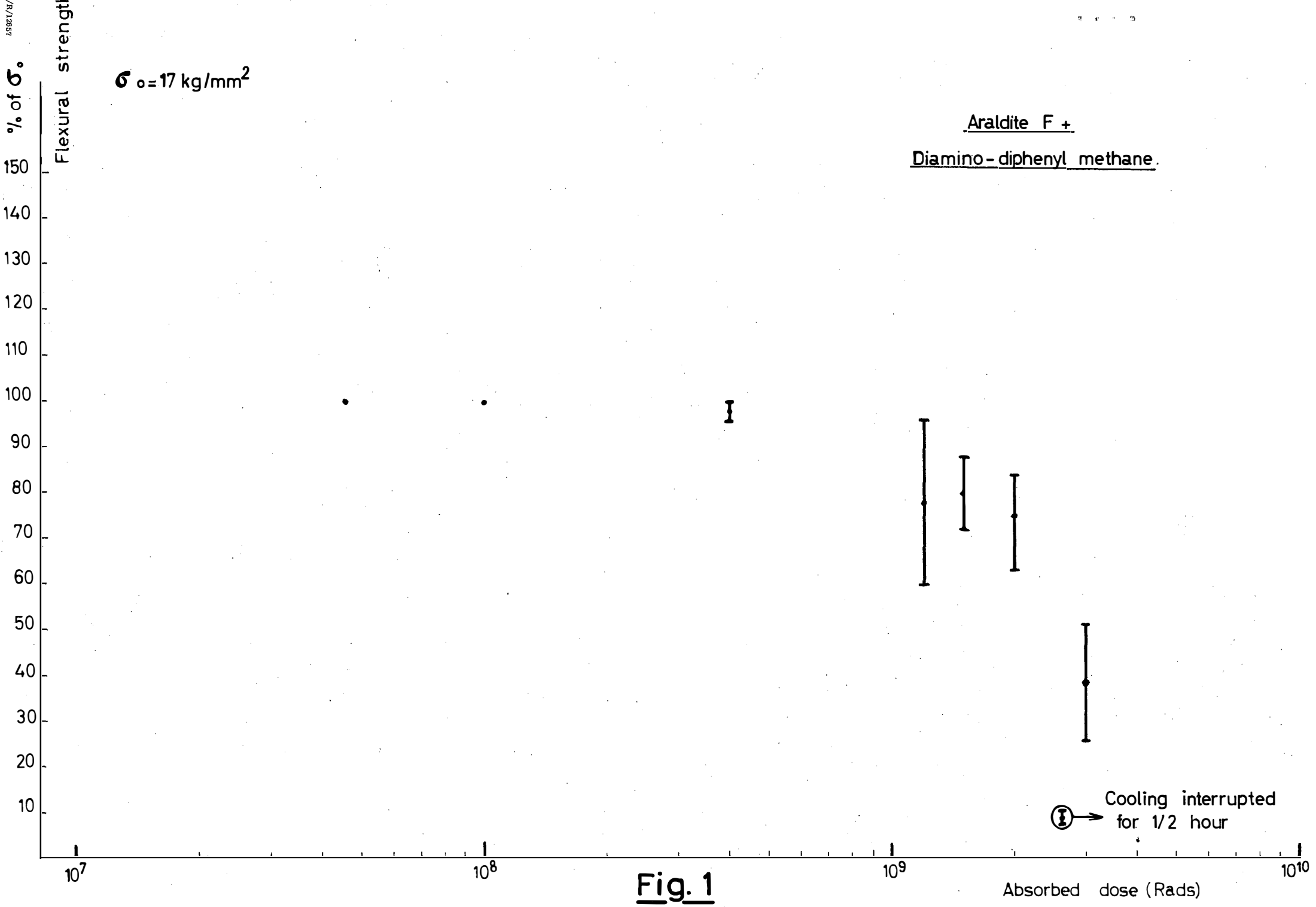
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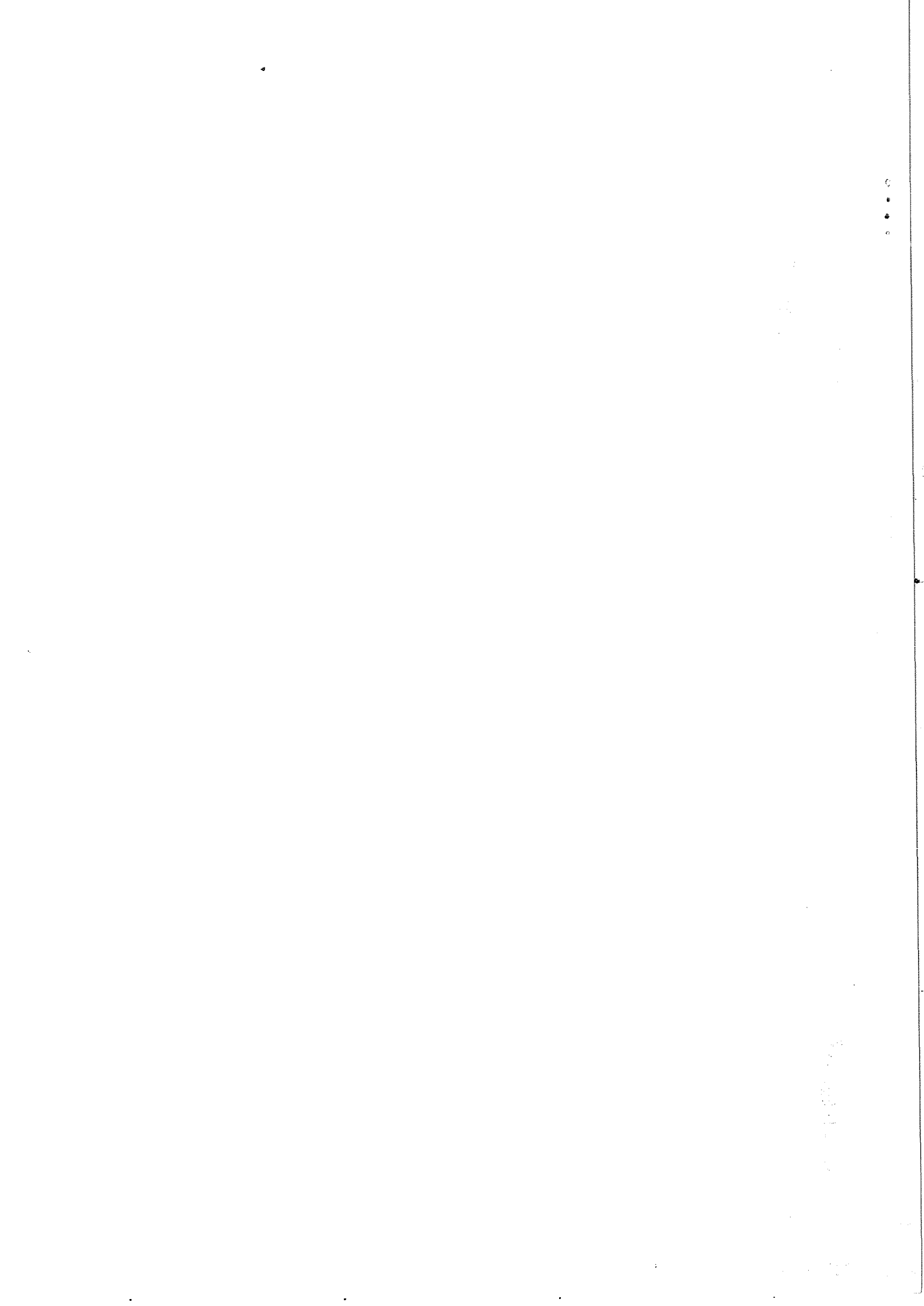
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Flexural strength

% of σ_o

$\sigma_o = 13 \text{ kg/mm}^2$

Araldite F +
Phthalic anhydride.

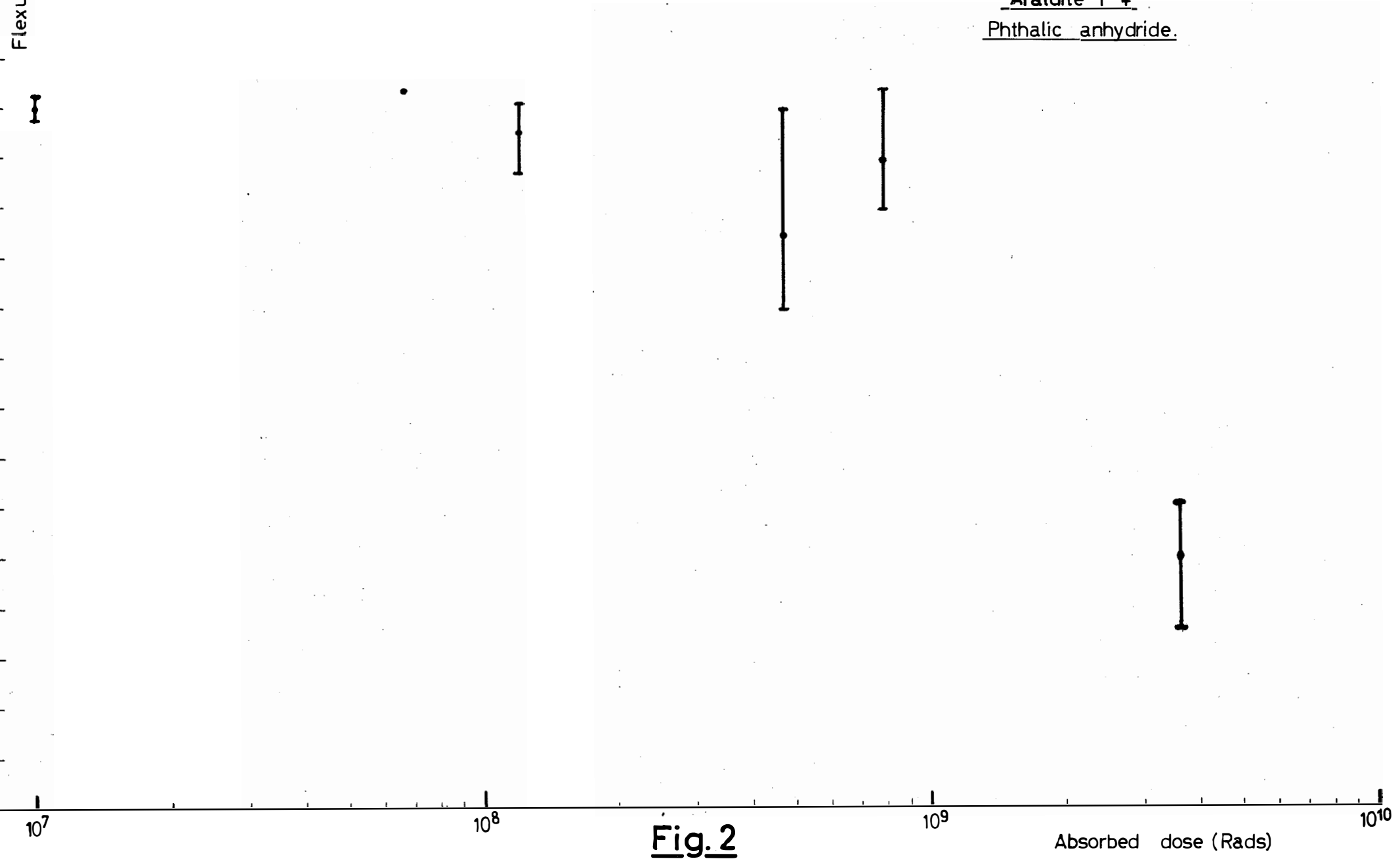


Fig. 2

Absorbed dose (Rads)

1000

1000