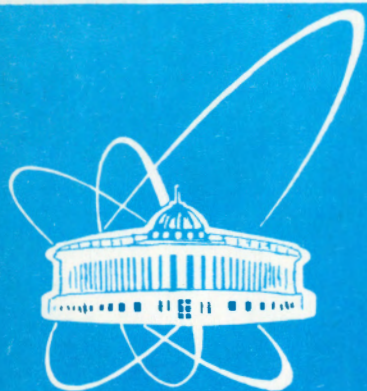


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NEW RADIATION STABLE AND LONG-LIVED
PLASTIC SCINTILLATORS

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INTRODUCTION

The main parameters of plastic scintillators that need to be improved for the SDC detector of the SSC are radiation stability and environmental aging. The traditional direction of research to improve rad hardness and aging is to search for new and better primary and secondary dopants emitting in the blue region [1], and to synthesize new polymer matrices [2]. The radiation stability of standard scintillator compositions (styrene, 2% p-terphenyl and 0.1% POPOP) is only 1 to 2 Mrad. Adding a CH₃ group to the benzene ring of polystyrene increases the annealing rate 1.3 to 1.5 times, but immediately after the irradiation the rad hardness is decreased. Recently progress has been made using the techniques of enhanced diffusion [3] and green emitting dyes [4]. New rad hard plastics lose no more than 10% of their light output after 10 Mrad and such plastics can operate for 10 to 20 years in the Supercollider. During such a long time, aging of the scintillator by oxidation and crazing becomes important. The former causes light loss by yellowing and the latter by scattering. The main goal of our investigations is to increase rad hardness and to develop methods of accelerated aging that can be used to test candidate scintillators.

EXPERIMENTAL

Samples are prepared by thermal initiation of polymerization of a vacuum distilled monomer at 120 to 140°C for about 10 hours, then increasing the temperature to 160°C for 2 days. The concentration of residual monomer in the samples was about 0.8%. Samples were cut and polished into cylinders with a diameter of 16 mm and a height of 10 mm. Light output is measured relative to a crystal of anthracene of the same size. Irradiation was by gamma rays from Co⁶⁰ to a dose of 2.8 Mrad at a dose rate of 1 krad per minute. Transmission spectra were measured on a Specord UV-VIS spectrophotometer relative to air. Samples from polymer were made by mixing the additives with polystyrene pellets in a mixing extruder at 160°C and injecting into a metal mold. The main goals of the experimental design were to increase rad hardness by

1. optimizing the concentration of secondary fluors;
2. synthesizing new secondary dopants and screening them for effectiveness;
3. synthesizing special primary dopants;
4. increasing the concentration of the primary dopants;

5. investigating methods of modification of the polymer structure, especially the molecular weight and molecular weight distribution;
6. adding antirads, stabilizers and antioxidants;
7. enhancing the diffusion rate of the base plastic.

OPTIMIZING THE CONCENTRATION OF THE SECONDARY LUMINOPHOR

As has been shown in numerous investigations [5,6], one of the main non-rad hard components of standard plastic scintillator is POPOP. Figure 1 shows the dependence of rad hardness on the concentration of secondary dopant. The optimum concentration is in region of 0.01 to 0.02%. Figure 2 shows that the residual transmission after irradiation decreases steadily with increasing concentration of POPOP.

SYNTHESIS AND SCREENING OF SECONDARY LUMINOPHORS

We have tested 200 luminophors in compositions based on styrene and using p-terphenyl as the primary luminophor. These secondary additives belong to the following chemical groups:

1. naphthalic acid derivatives (samples 330, 391, 397 in Fig.3);
2. oxazoles (samples 399 and 546 in Fig.3);
3. pyrazoles;
4. triazoles;
5. benzoxazoles,
6. naphthazoles.

The standard composition of styrene with 2% p-terphenyl and 0.1% POPOP is shown in samples 406 in Figure 3 and 529 in Figure 12. The difference between them may be due to some variation in the preparation of the samples. The first three groups listed above are the most radiation hard. We now think that it is not very probable that a secondary luminophor emitting at around 420 nm can be found that is more rad hard than POPOP or tetraphenylbutadiene (TPBD).

THE EFFECT OF PRIMARY DOPANT CONCENTRATION ON RADIATION HARDNESS

We began this investigation because of the following two points. First, reports in the literature show that at a dose of 3 to 5 Mrad the concentration of stable radicals reaches a few percent. From an investigation of the spectral properties of these stable radicals, we can conclude that their absorption

competes with the energy transfer from the polymer to the primary dopant. Second, it has been shown that the radiation resistance of p-terphenyl alone is about 100 Mrad. Therefore an increase in the p-terphenyl concentration in a composition should not decrease the radiation hardness as we observe with POPOP. And therefore, increasing the p-terphenyl concentration relative to the concentration of the stable radicals should shift a greater proportion of the energy transfer from the base plastic into useful light. Any solubility problems with the high concentration of p-terphenyl seem to have been overcome by the higher temperatures we used in polymerization or extrusion. We cannot yet prove that these high concentration scintillators will be stable over time or if some precipitation may occur. As yet no cloudiness has been seen. Figures 4,5,6 show the increase in radiation hardness with increasing concentration of p-terphenyl in the range of 4 to 6% immediately after irradiation. Similar results are shown for other terphenyl isomers in Figures 7,8 and 9. From Figures 4 through 9, also immediately after irradiation, we see that some parameters decrease in the high concentration region of p-terphenyl particularly the transmittance; we attributed this to contaminants. We investigated this by trying different samples of commercial p-terphenyl and one specially purified one. The purification was done by first irradiating the p-terphenyl and then zone refining it. In this case a more transparent and rad hard scintillator was obtained. Samples with an increasing concentration of p-terphenyl did show increasing rad hardness, but samples with m-terphenyl did not (Fermi unpublished measurements of Ukrainian samples). The effect of polymer structure (Figure 10) shows the dependence of rad hardness on p-terphenyl concentration for samples made by different methods. The lower curve labeled 1 is data from samples prepared by polymerization of monomer and the upper curve labeled 2 is data from samples made by pressure molding from pellets of polymer. The rad hardness of the samples molded from polymer is consistently higher. The method of preparation of the samples also influences the light output as is shown in reference 8, a paper being presented at this conference by F.Markley et al., where the light output of samples from polymer is nearly 1.5 times that of the samples from monomer. The data of Markley do not show greater rad hardness for samples from polymer, but the specific formulations used were very different from those used at Kharkov.

INFLUENCE OF POLYMERIZATION METHODS

It must be added that different methods of polymerization also influence scintillator parameters. Figure 11 shows the dependence of light output on length for two different scintillator, one made from styrene and the other from vinyltoluene. It is unusual that the light output from the styrene based scintil-

lator should be 1.3 times the light output of the scintillator based on vinyltoluene. The scintillators were made in Kharkov and measured in Pisa in the laboratory of G. Bellettini. The variations in light output of scintillators made by different methods or with materials of different purity may be explained by a difference in concentration of the sites at which photochemical or photophysical reactions occur. Rad hardness may be influenced by radical recombinations that occur more efficiently at such sites [9], and light output by increased efficiency of energy transfer from excited states occurring at such sites [10]. It should be emphasized that the concentration of such sites may depend on the molecular weight distribution.

THE EFFECT OF STABILIZERS

The radiation resistance of a scintillator may be improved by the addition of small amounts of chemically active substances without changing the light output. Figure 13 shows that the metallo-organic stabilizer increases both radiation resistance and light output. It makes one of our best compositions on the basis of a combination of properties including mechanical ones.

THE EFFECT OF DIFFUSION ENHANCERS

The introduction of large amounts of low molecular weight fillers to facilitate diffusion in the polymer base accelerates annealing. We have attempted to improve rad hardness by using polyphenyloxides which has been proposed in [8] (see Figure 12A), methylnaphthylene (see Figure 12B) and oxibenzole (see Figure 12C). The best results were obtained with 20% diphenyloxide, with or without stabilizer. This composition retained 91% of its initial output after 2.8 Mrad irradiation in air. We believe the diffusion enhancing technique is the best method of improving scintillator rad hardness.

ACCELERATED AGING TESTS OF PLASTIC SCINTILLATORS

Environmental aging is a basic parameter characterizing long time stability even without the effect of radiation. Such aging may be seen as yellowing or clouding or crazing of the surface or cracking in depth. In all cases the light output decreases. It is important to develop a prognostic tool for sample stability and to optimize the manufacturing and post-treatment conditions to produce stable scintillators. In developing an accelerated aging test it is important to achieve the maximum likeness to the natural degradation processes.

We assume that polystyrene aging is due to the following mechanisms:

1. Thermooxidative processes resulting in the creation of peroxides which absorb in the region of the scintillating radiation.
2. Mechanical degradation due to chemical stress crazing which causes surface cracks that disrupt light transmission.
3. Diffusion of low molecular components of the formulation which can cause both surface and internal defects. In this case yellowing, clouding of the interior or the surface, and cracking can arise.

The above mechanisms lead to changes in the scintillation efficiency which in any realistic case are due to one or at most a few parameters. These parameters determine the practical usefulness of any scintillator composition. We have investigated the effect of the following four parameters on the efficiency of polystyrene scintillators:

1. The influence of temperature for long times on the light output.
2. The combined influence of high temperature and high humidity on the appearance of cracks. This makes it possible to increase both thermaloxidative processes and thermomechanical ones.
3. The combined effect of high temperature and water immersion. This accelerates the formation of under-surface crazes by a factor of 6 compared to high humidity, and makes possible the substitution of a simple weight gain measurement for the laborious microscopic measurement of craze numbers.
4. The effect of thermal shock after a long soak at high temperature to stimulate cracking.

The results of these tests are given below.

1. Heat aging

Polystyrene samples of the standard composition were made into cylinders with a diameter of 40 mm and a thickness of 40 mm. They were subjected to elevated temperatures in the range from 45 to 85°C. These temperatures are below the glass transition temperature of the standard sample. Figure 14 gives the time dependence of the parameter G , where $G = C/C_0$ and C and C_0 are the light output before and after heating respectively. We define the critical time to be the time when the light output has decreased by 10%. The lifetime at 20°C is determined from an Arrhenius plot, where the logarithm of the critical time is inversely proportional to the temperature.

Analytically, the lifetime is given as:

$$\ln \tau_{20} = \frac{T_i T_j \ln(\tau_i / \tau_j) \left(\frac{1}{T_{20}} - \frac{1}{T_i} \right)}{T_i - T_j} + \ln \tau_i$$

where T_i and T_j are the temperatures of two arbitrary elevated temperature tests, and the τ 's are the corresponding critical times. The extrapolated lifetime

for a standard sample determined in this way is 11.5 years which is in excellent agreement with the lifetime of 12 years actually measured at 20°C. This method allows us to determine the maximum value for residual monomer (RM) which yields a lifetime of 10 years. Figure 15 is a graph of lifetime versus residual monomer content in percent.

2. Heat and humidity

The samples in this test were held at temperatures from 30 to 50°C at a relative humidity of 95%. Figure 16 shows the number of crazes found versus exposure time at 3 different temperatures. The critical time in this test is defined as the time until the appearance of the first craze in the field of view of a microscope with a magnification of 8 times. The lifetime at 20°C and 95% is defined by a graphical extrapolation from the curve of log (critical time) versus inverse temperature. This is measured as 1.5 years for a sample 40 mm in diameter and 30 mm thick which was prepared by polymerization at 170°C. It is likely that the lifetime is dependent on the sample history, in particular on the cutting conditions, because the migration rate of water into the sample depends on the number of surface and volume defects in the sample.

3. Heat and water immersion

The samples in this test were immersed in distilled water at temperatures ranging from 40 to 70°C. The critical time is defined and the lifetime determined as in the heat and humidity test. The table gives the critical times measured at four different temperatures. A new critical time can be defined as the time to reach a particular gain in weight (in our case 0.004 g) by using the data shown in Figure 17, which shows the measured weight gain as a function of time for 3 different temperatures. The weight gain is much easier to determine than the appearance time of crazes.

4. Thermal soak and shock

We have made a quantitative measurement of the number of defects which appear on the surface of a sample after a thermal shock from a soak temperature to a temperature of 20°C. Figure 18 gives the number of defects found versus the soak temperature. The time of soaking was the same for all samples. We did not find the expected relationship between the number of defects and the soak time.

Table. The dependence of τ_{cr} and the operation time PS calculated by thermal aging method under different contents of RM in PS

| RM, % | τ_{cr} , days | Operation time, years |
|-------|--------------------|-----------------------|
| 0.5 | 45.0 | 14.5 |
| 1.0 | 23.0 | 7.4 |
| 1.5 | 16.5 | 5.3 |
| 2.0 | 11.0 | 3.5 |
| 2.5 | 10.5 | 3.4 |

We therefore feel that a more objective method is needed to evaluate the number of surface defects.

CONCLUSIONS

It is found that the light output and radiation hardness of the scintillators prepared from pellets, is greater than that of scintillator prepared from monomer. This may be explained by a sharper distribution of molecular weight found in the polymer pellets. It is shown that a concentration of pT of 4—6% of the total composition is optimum for radiation hardness. Increasing the concentration of pT increases the annealing rate of the scintillator. A new scintillator with polystyrene base, containing 2% pT, 0.02% POPOP, and 20% new diffusion enhancer retains 91% light output immediately after 3 Mrad irradiation in air. We conclude that the diffusion enhancing technique is the most effective direction for improving radiation hardness. The effects of high temperature, high humidity, water immersion, and temperature shock were investigated and are proposed for accelerated aging of plastic scintillators.

PST + 2%PT + PCPOP(LAF)
 d16 X 10mm; γ -ray ^{60}Co , 2.7 Mrad.
 Immediately after irradiation in air.

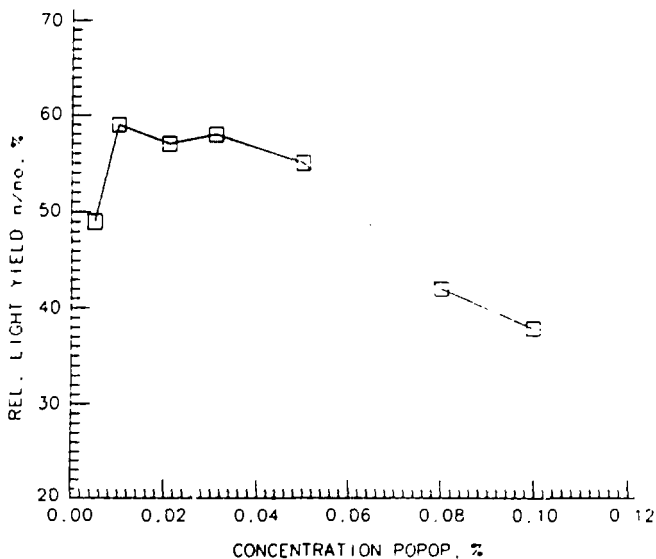


Fig. 1

PST + 2%PT + POPOP(VAR)
 d16 X 10mm; γ -ray ^{60}Co , 2.7 Mrad.
 Immediately after irradiation in air.

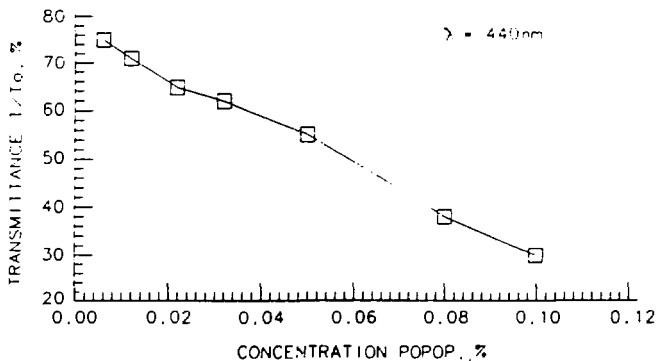


Fig. 2.

LIGHT YIELD,
% OF ANTR.

2.9 MRAD Co-60

— No
 ■ — 1/2
 ▨ — 1/4 No

406 - STANDARD
COMPOSIT CH

330, 331, 397 - NAPHTHAL C
ACID DERIVATIVES

399 546 - DAZOLES

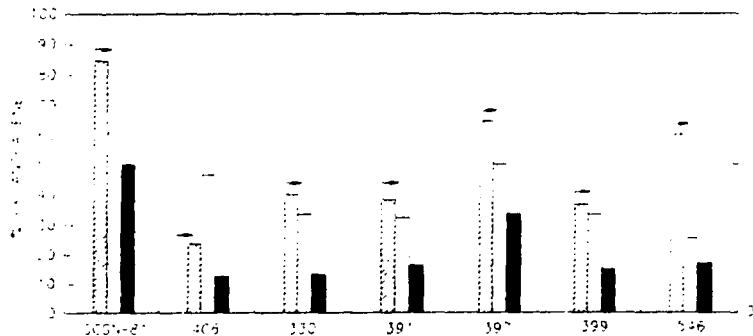


Fig. 3

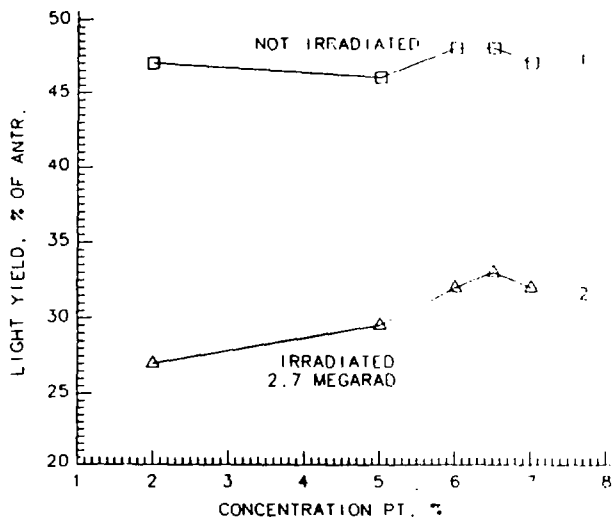


Fig. 4

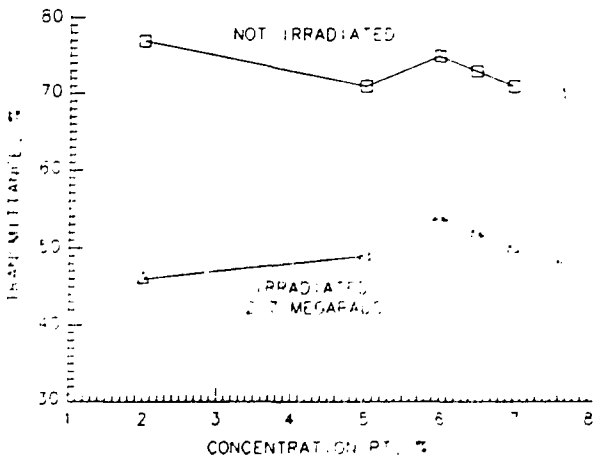


Fig 5

PST + PT (VAR) + 0.02% P0P0P
 d16 X 10mm; γ -ray ^{60}Co , 2.7 Mrad
 Immediately after irradiation in air

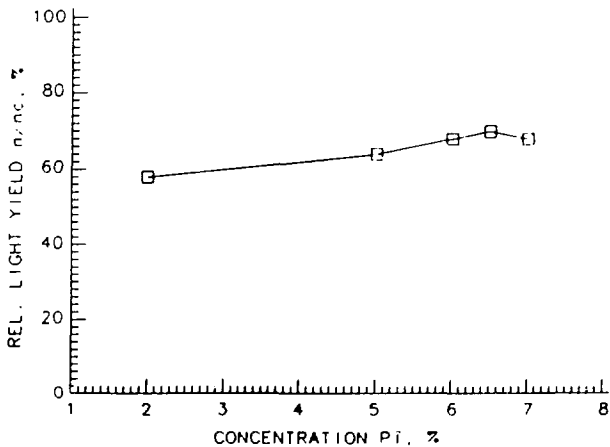


Fig 6

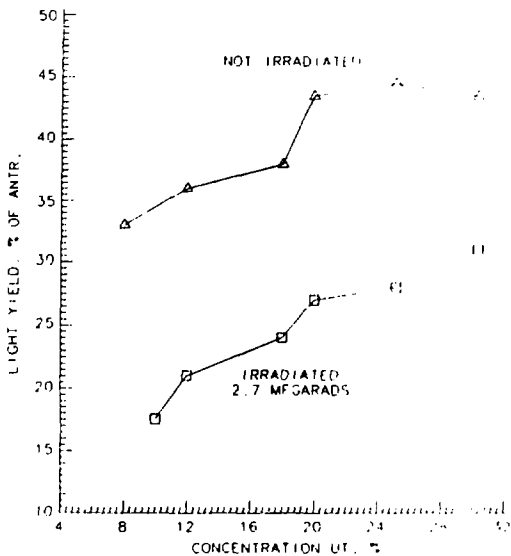


Fig.7

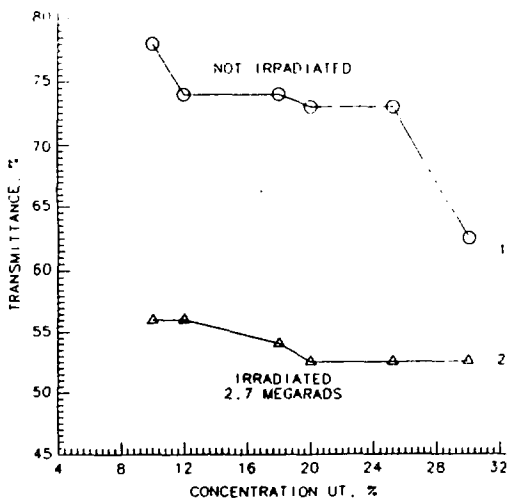


Fig.8

PST + UT(VAR) + 0.02% POPOP
 d16 X 10mm; γ -ray ^{60}Co , 2.7 Mrad.
 Immediately after irradiation in air

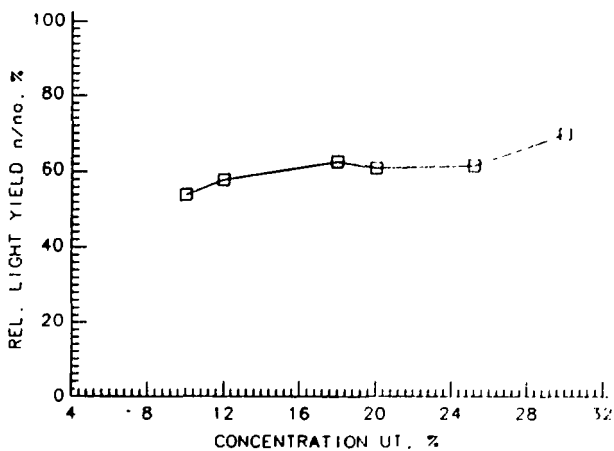


Fig.9

PST + PT(VAR) + 0.02% POPOP
 d16 X 10mm; γ -ray ^{60}Co , 2.7 Mrad.
 Immediately after irradiation in air.

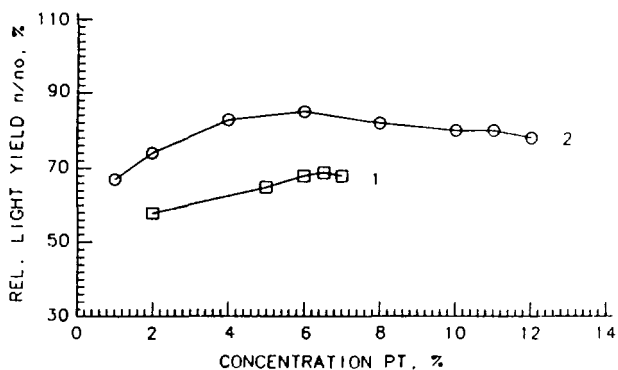


Fig.10

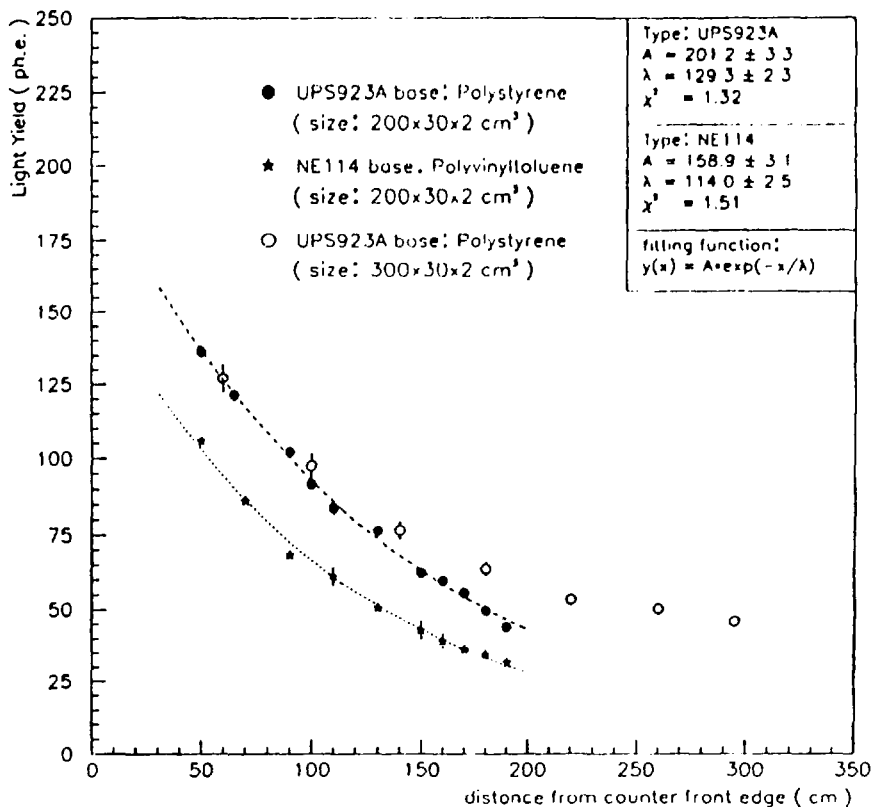


Fig.11

LIGHT YIELD
% OF ATRP

□ - N₂
■ - N₂
▨ - N₂O

2.8 MRAD Co-60

529 - PT(2%) + POPOP(0.02%)
 521 - PT(2%) + POPOP(0.02%) + St,N24(0.01%) + A
 522 - PT(2%) + POPOP(0.02%) + St,N24(0.01%) + B
 523 - PBD(2%) + POPOP(0.02%) + St,N24(0.01%) + A
 525 - PT(2%) + POPOP(0.02%) + St,N24(0.01%)
 SCSN-81-PHB(1%) + TBBT(0.02%) + St(0.02%)

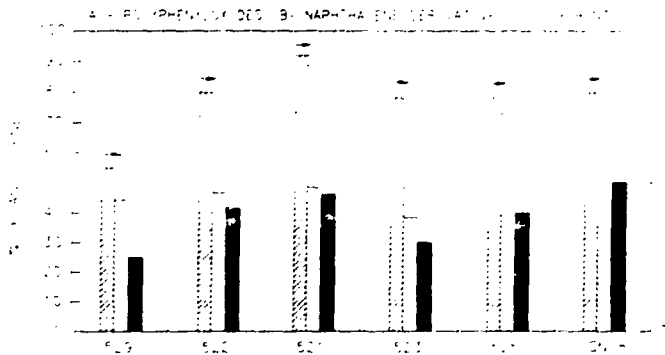


Fig. 12

LIGHT YIELD
% OF ATRP

□ - N₂
■ - N₂
▨ - N₂O

2.8 MRAD Co-60

528 - PT(2%) + POPOP(0.02%)
 529 - PT(2%) + POPOP(0.02%)
 538 - PT(5%) + N172(0.02%)
 592 - PT(2%) + POPOP(0.02%) + St,N24(0.02%)
 SCSN-81-PHB(1%) + TBBT(0.02%) + St(0.02%)
 St,N24 - METALORGANIC STABILIZER

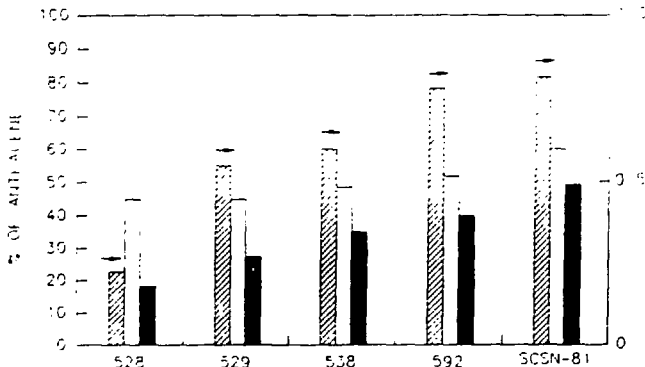


Fig. 13

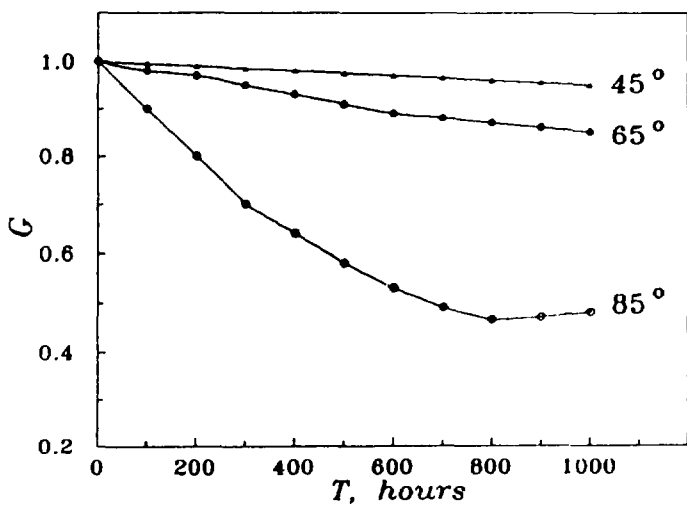


Fig.14

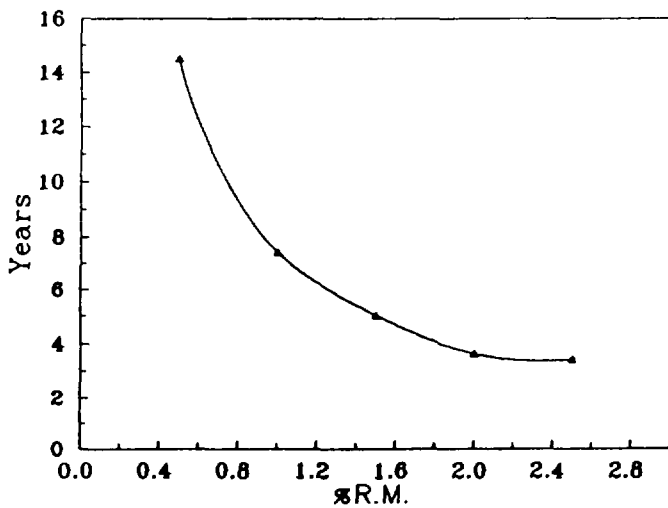


Fig.15

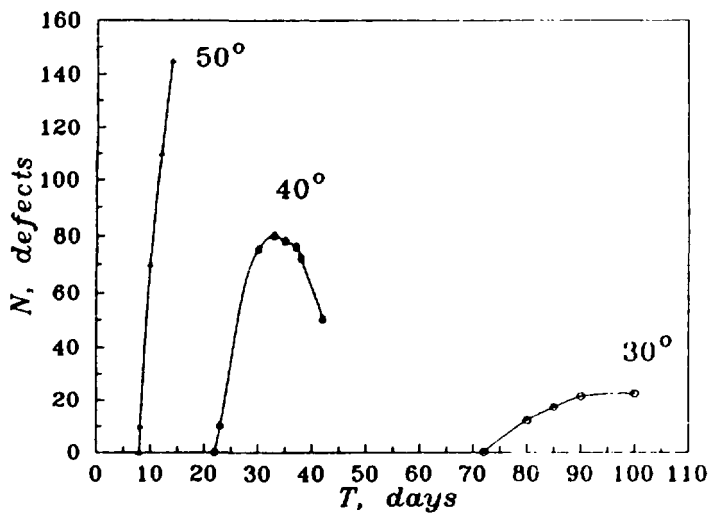


Fig.16

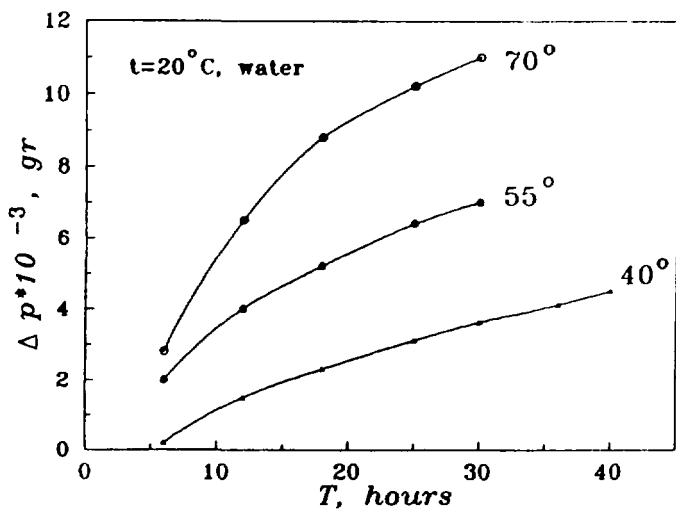


Fig.17

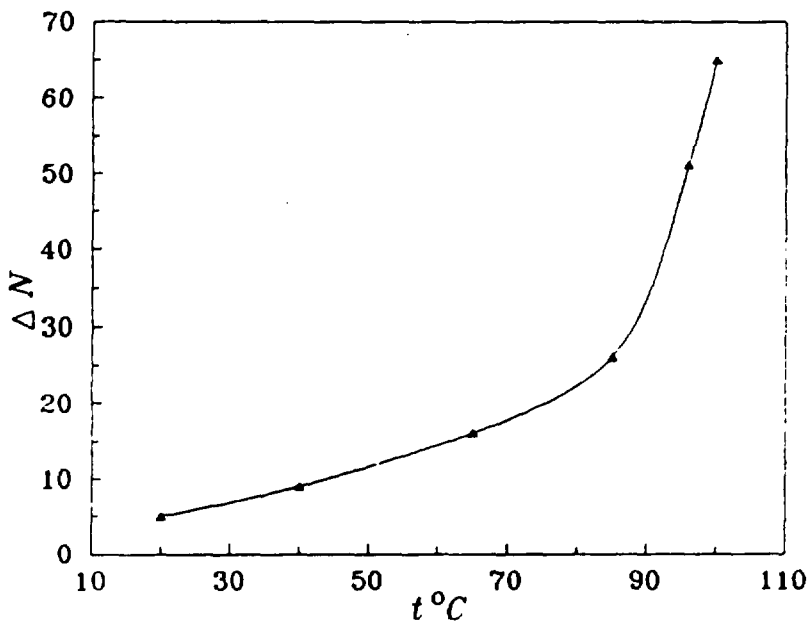


Fig.18

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