

◀Technical Report▶ A Study on the Preparation of Tritium Luminous Compound

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Abstract

For the syntheses of tritium labelled polystyrene, the basic material for the preparation of tritium luminous compound, various methods of labelling such as Tesla discharge, Wilzbach exposure, gamma irradiation, and U.V. irradiation were compared in view of getting high specific activity-product. The obtained polystyrene-T(G) by the method of Tesla discharge and by the method of U.V. irradiation had specific activity of 1~1.2 mCi/mg, and these two methods were the most encouraging. Mixing of 1 part of polystyrene-T(G) with 4 parts of ZnS:Cu phosphor, in weight, appeared to be the most suitable ratio in the preparation of luminous compound in luminosity point of view. When 30 mg. of obtained luminescent mixture was applied on steel plate by using 1 ml. of the selected binder (*i. e.*, 1 g of commercial varnish in 100 ml. of benzene) the luminosity maximum was ca. 20 micro Lambert. The prepared luminous compound was confirmed to be practically applicable for mine marker or dark-room light source.

요 약

트리튬 표지 형광도료의 원료인 고 비방사능의 트리튬 표지 폴리스타이렌을 얻기 위하여 테슬라 방전법, 윌즈바흐 노출법, 감마선 조사법, 자외선 조사법등 여러 방법들을 비교 검토하였다. 테슬라 방전 또는 자외선 조사법으로 얻은 polystyrene-T(G)의 비방사능은 1~1.2 mCi/mg로써 다른 방법에 의한 생성물의 값보다 높았다. Polystyrene-T(G)와 ZnS:Cu 형광체를 무게비로 1:4가 되게 혼합하면 광도가 가장 컸다. 30 mg의 형광도료 혼합물을 1 ml의 바인더(시판 니스 1g을 100 ml의 벤젠에 녹인 것)를 써서 바르는 경우 최대 광도는 약 20 μ L이었으며 갱내 표지판이나 암실내 광원으로 유효하게 사용될 수 있음을 확인하였다.

1. Introduction

It is well known that many materials both organic and inorganic can be caused to

luminesce to a visually detectable extent under the influence of ionizing radiation. Inorganic phosphors in particular are characterized by such behavior and have been

extensively employed in the commercial production of luminous coating materials of various types. The early known one is the coating of watch-dials with phosphor containing radium. The alpha rays emitted by radium interact with the phosphor molecules (eg. ZnS) to a luminescent state through a certain mechanism¹⁾.

Radioactive strontium has also been mixed with inorganic phosphors of various types to provide artificial light sources of adequate luminosity. However, the use of such Ra or Sr-90 results definite radiation hazard due to the exceedingly high penetrating activity of the corpuscular radiation emitted thereby, and accumulation of these isotopes in the bony organs. A further limitation on the industrial use of both Ra and Sr-90 activated phosphor resides in the state at which the phosphor material is destroyed by the densely ionizing particles, and consequent luminosity diminutions. ³H and ¹⁴⁷Pm are recently appeared to be adequate sources of the beta radiation. To obtain the highest specific activity, namely the greatest light emission per unit weight of the luminescent mixture, it is necessary to introduce chemically into the organic compound a high content of beta emitters such a tritium.

A number of methods are known for chemically introducing tritium into organic compounds; 1) simple tritiation such as addition to double bond, 2) recoil labelling, 3) simple Wilzbach exposure and 4) tritiation under ionizing radiations. It is known that the applicability of the methods of 1) and 2) is limited to some compounds which are facile by chemical or recoil induction. Consequently, to obtain highly tritiated polymer base such as polystyrene-T(G) which may be adequate for a component of the luminescent mixture the author has adopted the methods of

3) and 4). The basis of the Wilzbach exposure is the hydrogen isotope exchange accomplished through the activation or ionization of organic compound by the radiation emitted from tritium which results radicals being formed with which the tritium atoms can be combine. This exchange reaction can further be accelerated by ionizing radiations such as U. V. light, gamma ray, Tesla or simple high voltage discharges. The detailed literatures concerning tritium labelling on polystyrene via above methods are hardly available. Only a patent specification²⁾ notices the outlines and possibilities. Thereupon, the main objectives in present study are stressed on obtaining tritium labelled polystyrene of high specific activity and determining the optimum mixing ratio of the obtained polystyrene-T(G) with ZnS:Cu phosphor as well as choosing suitable binder material for preparation of tritium luminous compound.

2. Experimental

(1) Tritium Labelling on Polystyrene

a) By Wilzbach exposure³⁾

200 mg of polystyrene powder obtained through radiation polymerization of pure monomer (WAKO), after careful distillation under reduced pressure, was loaded in the reaction flask (Fig. 2A) settled in the high vacuum line (Fig. 1). The tritium gas ampoule (20 Ci, 4 ml., R.C.C. Amersham was attached to one end of the line, and the whole system was evacuated to ca. 10^{-5} mmHg. Being closed the main stopcock the break seal of the tritium gas ampoule was broken with a magnet and an iron piece. The gas was transferred to the reaction vessel by manual operation of the Toepler pump. The pressure of the tritium gas in the reaction vessel was 0.3 atm. which could be determined by compressing the tritium atmosphere filled

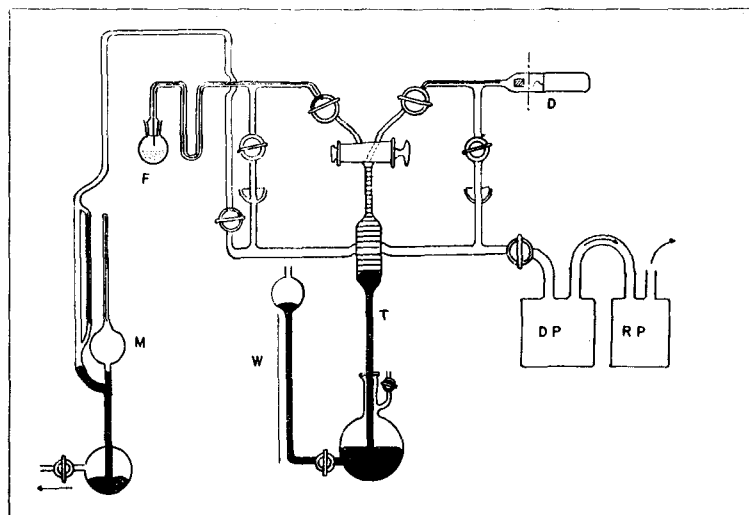


Fig. 1. A high vacuum line for manipulation of tritium gas

- | | |
|------------------------|--|
| D: tritium gas ampoule | W: manual controller for mercury level |
| F: reaction vessel | DP: oil diffusion pump |
| M: McLeod gauge | RP: rotary pump |
| T: Toepler pump | |

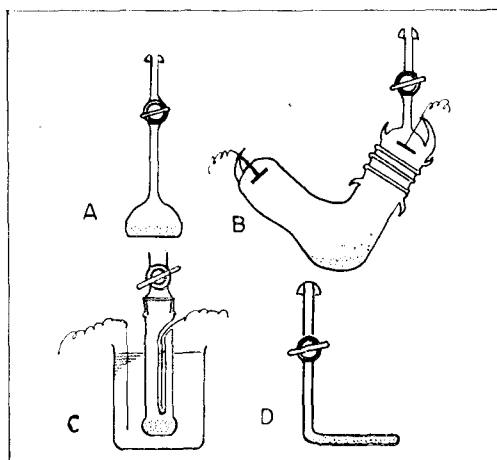


Fig. 2. Reaction vessels

- A: for Wilzbach exposure or for Tesla discharge
 B: for simple high voltage discharge
 C: for silent electrical discharge
 D: for cobalt-60 gamma irradiation or U.V. irradiation

in the upper end of the Toepler pump and by reading the difference of mercury column levels between the mercury storage bulb line and the Toepler pump line. The whole setting was allowed to stand still for 10 days or so. After definite duration the tritium gas in the reaction flask was withdrawn by means of

Toepler pump. The flask is detached from the line and a fraction of the content was weighed and dissolved in benzene for radioactivity counting through liquid scintillation (Fig. 3). The fraction remained was used for mixing ratio determination with the ZnS:Cu phosphor.

b) By Tesla discharge²⁾

In specially designed flask, 200 mg of polystyrene powder was charged. The experimental manipulation was similar to that of Wilzbach exposure except the additional 50 KV Tesla discharge during the contact of the reactants. After definite time of discharge a fraction of the content was taken out and its activity was counted as previously (Fig. 4)

c) By simple high voltage electrical discharge²⁾

The experimental manipulations were similar to that of Wilzbach exposure except the additional 15 KV electrical discharge during the contact of the reactants by using neon transformer. The reaction vessel used is represented in Fig. 2B. In a definite time

intervals a fraction of the content was taken out and its activity was counted as previously. A series of tritiation experiment was also performed with modified method of electrical discharge, so called silent electrical discharge, using the reaction vessel illustrated in Fig. 4, C).

d) By ^{60}Co gamma irradiation²⁾

70 mg. of polystyrene powder and 0.1 atm. of tritium gas was charged in the reaction tube illustrated in Fig. 2D. The samples in the reaction tubes were irradiated by ^{60}Co gamma ray under the dose rate of 340 rad/sec varying the total dose (Fig. 5).

e) By U. V. irradiation²⁾

The conditions were similar to that of gamma irradiation but in this case U. V. light of wave length 2537 Å was irradiated varying time (Fig. 6).

The results of tritiation of polystyrene in various methods are summarized in Table 1.

(2) Determination of Mixing Ratios and Luminosity

The polystyrene-T(G) obtained by the Tesla discharge method was subjected to the mixing ratio determination. The polystyrene-T(G) was mixed with ZnS:Cu phosphor (Dai Nippon Toryo Co.) in various ratios. 30mg. of the mixtures were finely ground and coated

on the surface (0.5 cm × 1.3 cm) of each stainless steel block (0.5 cm × 1.3 cm × 1.3 cm) by using 1 ml of kneading agent (binder) made of 1 g of commercial varnish and 100 ml of benzene. The sample coated stainless steel blocks were inserted into the cell holder of the fluoroglass dosimeter (Aloka FGD-3B). To eliminate the extra excitation of the phosphor by light energy the samples in the holder were kept in darkness for at least 1 hr. After the constant current being confirmed the luminosity of each sample was read in mA. The luminosities of the tritium luminous compounds of TRL-40 and TRL-55 (Radiochemical Centre, Amersham) of which maximum luminosity in micro Lambert was 40 and 55, respectively, were also measured in mA. In such a manner the luminosities of the luminous compounds prepared in various ways could be expressed in micro Lambert (Fig. 7, 8, 9 and Table 2).

(3) Selection of Binder

The polystyrene-T(G) and ZnS:Cu phosphor were mixed in the weight ratio of 1:4 according to the result obtained from the afore-described experiment for mixing ratio determination. 300 mg of the mixture was kneaded with 1 ml of a pure solvent or with the solvent containing definite amount of commercial varnish and applied on the surface (0.5 cm ×

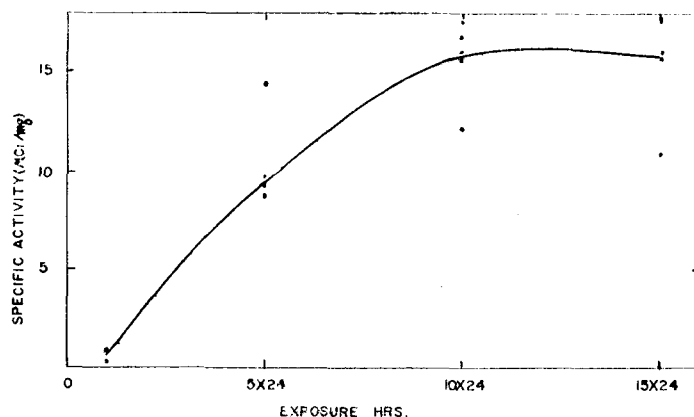


Fig. 3. Tritiation of polystyrene by Wilzbach exposure

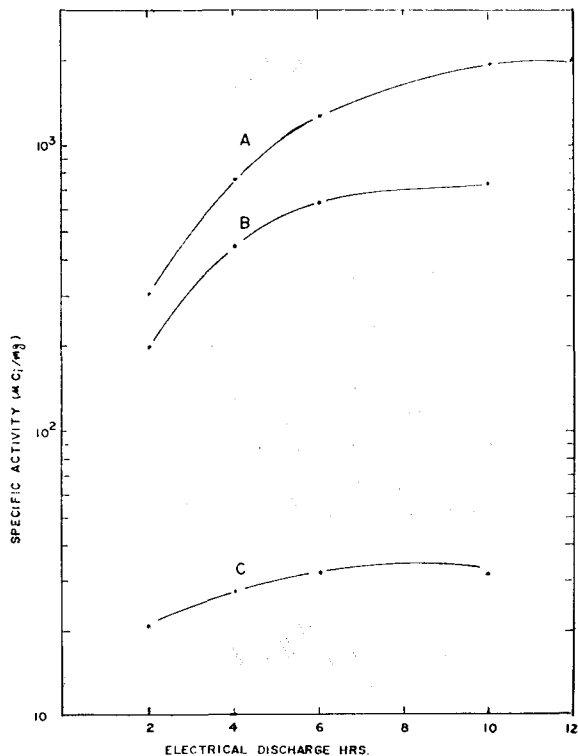


Fig. 4. Tritiation efficiencies in the various electrical discharge methods

- A: Tesla discharge,
- B: simple high voltage discharge
- C: modified silent electrical discharge

1.3 cm) of the previously described blocks. The luminosity decreases owing to the presence of binder were also measured using fluoroglass dosimeter. After the luminosity decreases were measured the same blocks were dropped on the wood-plate freely from the top of the vertically stood glass tubing of 120 cm long. The average weight decreases were measured to ascertain the binding force of the applied binder (Table 3).

3. Results and Discussion

For preparation of tritium luminous compound, securing high specific activity-polymer base is the most essential as far as the luminosity is proportional in some extent to the intensity of excitation of phosphor by radiation. The experimental results indicate that the Tesla discharge or U. V. irradiation method is preferable to the others.

Wilzbach exposure method gives quite low specific activity-product and the further disadvantage of this method is that it needs very long time of reaction since the exchange reaction in the method is only activated by

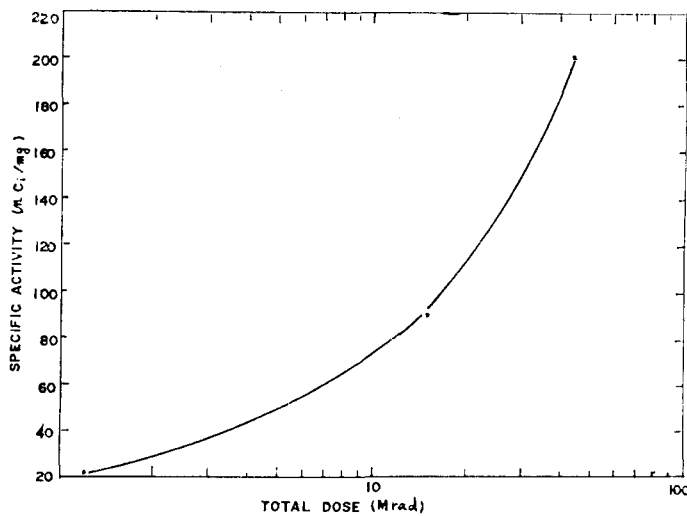


Fig. 5. Tritiation of polystyrene by Co-60 gamma irradiation under the dose rate of 340 rad/sec.

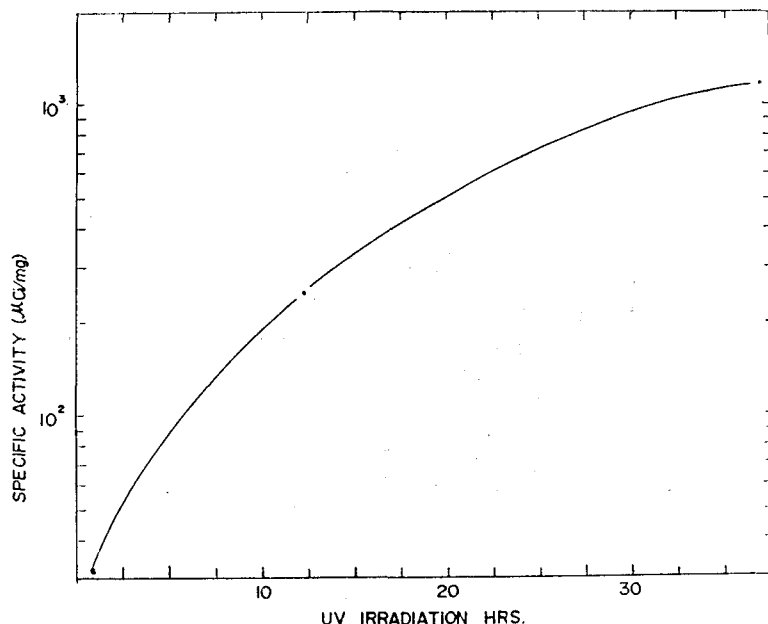


Fig. 6. Tritiation of Polystyrene by U. V. irradiation (wave length=2537Å)

the beta energy ($E_{max} = 0.018$ Mev) of tritium in situ of contact between the solid phase of polystyrene and the gas phase of tritium.

The simple high voltage electrical discharge method using neon transformer (H. V. $max = 15$ KV) results higher specific activity-product than the Wilzbach method. It means that the high voltage applied in the reaction system certainly accelerate the exchange reaction. The modified electrical discharge (silent electrical discharge) is rather worse than the simple high voltage discharge due probably to the discharge is not efficient. By 50 KV Tesla discharge for 10 hrs it was possible to get the product of which specific activity is as high as $1200 \mu\text{Ci/mg}$. ^{60}Co gamma irradiation under the dose rate of 340 rad/sec seems to be another efficient method, and even though the obtained data are insufficient to search the optimum dose for labelling it is still expected that the labelling efficiency will be increased with increasing total dose in some extent. In case of increasing total dose, however, significant degradation of polystyrene molecule will also be occurred. U. V.

Table 1. Tritium labelling on polystyrene

Mode of labelling	Poly-styrene (mg)	Tritium gas (atm)	Specific activity (Max.) in micro Ci/mg
Wilzbach exposure	200	0.3	16
Tesla discharge	150	0.2	1200
High volt. discharge	150	0.2	600
Silent electrical discharge	150	0.2	33
^{60}Co gamma irradiation	70	0.1	860
U. V. irradiation	70	0.1	1000

irradiation method seems to be more efficient than the gamma irradiation in view of simple manipulation. All of the methods applied are to make easy formation of free radicals from the polymer or from the tritium gas to accelerate the exchange. The wave length of the applied U. V. ray is 2537 Å. The energy will be ca. 110 Kcal/mole according to the following equation;

$$E = h\nu = h \times c / \lambda$$

$$E = N \times h \times c / \lambda = 28635 / \lambda (\text{m}\mu) = 28635 / 253.7 = 110 \text{ Kcal/mole}$$

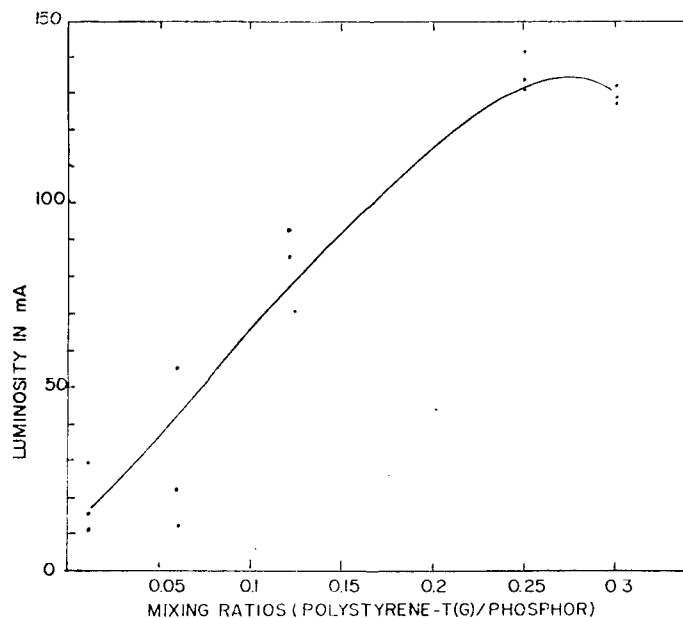


Fig. 7. Mixing ratios vs. luminosities

Therefore, the energy is sufficient to make free radical from the C-H bond in polystyrene since the average C-H bond energy is 99-100 Kcal/mole.

In the experiment for determination of optimum mixing ratio of polystyrene-T(G) with ZnS:Cu phosphor (Fig. 7) the luminosity is increased in wide range with increasing the ratio of polystyrene-T(G). Such a phenomenon is attributable to the low specific activity of polystyrene-T(G). It is certain that the mixing ratio will be varied with the variation of specific activity of the labelled polystyrene. The optimum mixing ratio of polystyrene-T(G)/ZnS:Cu phosphor=1/4 is obtained with the polystyrene-T(G) of which specific activity is ca. 1200 μ Ci/mg. It is reported that the mixing ratio of polystyrene-T(G)/phosphor=1/20 is optimum²⁾, but there is no comment on the specific activity of the polystyrene-T(G) and the kind of phosphor.

The luminosity for the the product obtained by Tesla discharge is approximately 20 micro Lambert which is only half of that of R. C. C.

Table 2. Apporximate luminosities of the products in micro Lambert

Origin of the luminous compds	(mA)	Luminosity micro Lambert(max.)
TRL-40*	283	40
TRL-55*	320	55
Tesla**	130	20***
U. V. **	[118	18***
Gamma-irrn. **	128	20***

* Luminosity in micro Lambert is standardized by Radiochemical Centre, Amersham, England

** The polystyrene-T(G), a component of the luminous compound is obtained by various labelling methods in this study

*** These are calculated as following; $L_{st} = L_{sm} \times L_{stl} / L_{stl}$

L_{st} ...luminosity in micro Lambert for the prepared products

L_{sm} ...luminosity in milli Ampere for the prepared products

L_{stl} ... luminosity in micro Lambert for TRL-40 or TRL-55

L_{stl} ...luminosity in milli Ampere for TRL-40 or TRL-55

product. Since the polystyrene-T(G) obtained by Tesla discharge method has the specific

Table 3. Selection of binder material for the luminous compound*

Composition of binder				Average weight decrease (%)	Average luminosity decrease(%)	Remarks
Inactive polystyrene (mg)	Commercial varnish (g)	Benzene(ml)	Chloroform (ml)			
2	1	100	0	10	48	fair
2	0	10	0	50	26	moderate
0	0	0	1	83	20	poor
0	1	100	0	16	40	fair
0	5	100	0	8	66	poor

* 30 mg of the prepared luminous compound (polystyrene-T(G)/ZnS, Cu phosphor=1/4) is kneaded with 1 ml of each binder. The polystyrene-T(G) is the product obtained by Tesla discharge, and its specific activity is ca. 1200 μ Ci/mg.

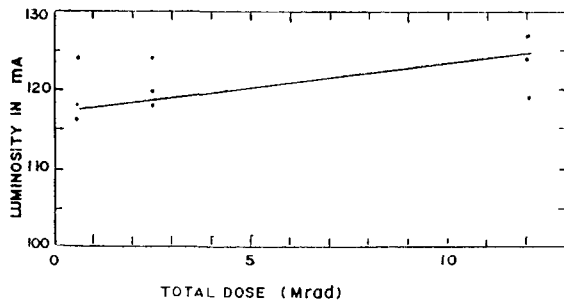


Fig. 8. Luminosity of the product obtained by gamma irradiation (polystyrene-T(G)/ZnS:Cu phosphor=1/4)

activity of 1200 μ Ci/mg, the highest, the luminosities of the luminous compounds made with polystyrene-T(G) obtained by other methods should certainly be lower than 20 micro Lambert. However, the differences in luminosities in micro Lambert are quite small. This fact seems unreasonable but it should

be remembered that the luminosity in micro Lambert is only approximate value (Table 3).

As far as the adhesivity is taken into account together with the degree of quenching the selected binder made of 100 ml of benzene and 1 g of commercial varnish is suitable in some extents. However, selection of non self-quenching and strongly adhesive binder should further be searched. If the amounts of varnish is increased the binding force will be stronger but severe quenching will be occurred.

4. Conclusions

(1) In comparison of the possibility of labelling tritium on polystyrene the Tesla discharge and/or U.V. irradiation methods are both effective.

(2) The optimum mixing ratio in the mixing of polystyrene-T(G) (sp. activity; 1200 μ Ci/mg.) with the ZnS:Cu phosphor is 1:4.

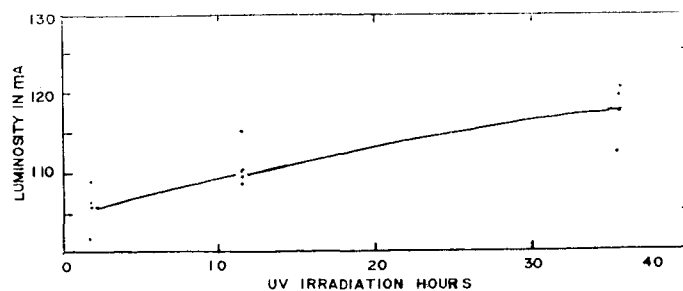


Fig. 9. Luminosity of the product obtained by U.V. irradiation (polystyrene-T(G)/ZnS:Cu phosphor=1/4)

(3) When 30 mg of the luminescent mixture is kneaded by using 1 ml of the selected binder (1g of commercial varnish in 100ml of benzene) the luminosity is about 20 micro Lambert.

(4) It is confirmed that the prepared luminous compound is practically applicable for mine marker or dark room light sources.

References

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