DEVELOPMENT OF RADIATION COLOR INDICATOR FILMS

M. C. R. Yamasaki, E. P. Araújo, E.S. Somessari and C.G. Silveira.
Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN-SP
Travessa R 400, Prédio do TE,
05508-900 Cidade Universitária, São Paulo, SP, Brazil
email: yamasaki@net.ipen.br

ABSTRACT

There are in Brazil gamma radiation and electron beam facilities using imported Yes-No films. The possibility of production in the country of this indicator film presents a great commercial interest. For this reason, IPEN developed a colored film that not only indicates whether it was irradiated or not but, through a continuous variation of the colors, this film can also indicate a minimum and maximum range of radiation dose absorbed during the process. This paper intends to describe the preparation procedure of this film and to show the final results obtained from the formulations studied.

1- INTRODUCTION

The preparation of a colored radiation indicator film is based on the radiation degradation of polyvinyl chloride (PVC). This polymer degrades under irradiation, releasing hydrochloric acid. The reaction can be written as:

$$(\text{— CH2 — CHCl —}) \xrightarrow[\gamma,\, e^-]{} (\text{-CH=CH-}) + \text{HCl} \qquad \text{(Eq.1)}$$

The hydrochloric acid concentration released during the irradiation depends on the absorbed dose. The addition of an acid sensible organic dye to PVC resin produces a film able to indicate, by a well defined color change, whether it was exposed to radiation or not. In this research, several combinations have been studied, aiming to obtain a film that presents a continuous and definitive color change depending on the amount of the absorbed dose.

The absorbed dose values utilized in industrial processes may range from some Gys, in genetic mutation of plants and food irradiation, to 1MGy employed in polymer crosslinking. In this project, a 10kGy to 70kGy dose range was chosen to be studied, but a variation on the concentration of components of each developed formulation may shift the dose range where a better color change is showed. This fact permits the film to be produced within a specific formulation to be used in determined irradiation processing.

2- MATERIAL and METHOD

Irradiation Sources. This research has been developed using a 1,5MeV and a 25mA industrial electron beam accelerator, Dynamitron II, manufactured by Radiation Dynamics, Inc., and a panoramic ^{60}Co source, initial Activity = 1.85 10^{14} Bq (May 1991).

Dosimetry. Cellulose triacetate films, calibrated in the ^{60}Co source with Fricke solution, have been used as a routine dosimeter.

Irradiation Conditions. The dose indicator films were irradiated in an electron beam accelerator under the following conditions: HVD = 40,8μA; E =0,630 MeV; Scan = 27%; L = 60cm; I = 1,0mA; v = 3,36 m/min and Dose Rate = 5 kGy/pass

Materials. PVC resin used in the dose indicator film preparation was PVC - Solvic (suspension), series 200, manufactured by Solvay. In this development were used the following pH indicators: Methyl Yellow 4-(dimethylamino)-azobenzol), Merck, PA; Orange IV (Tropaeolin 00), Baker, PA; Bromephenol Blue (3,3',5,5' tetrabromophenolsulfonphthalein), QM, PA; Bromocresol Green (3,3',5,5'tetrabromo-m-cresolsulfonphthalein), QM, PA.

A combination of cyclohexanone, Merck, PA, and methylethylcetone, Merck, P, was used as solvent of PVC resin. The pH of the ink obtained was modified by addition of some drops of trilaurylamine, Akzo Chemical, commercial grade.

FILM PREPARATION. PVC resin was dissolved in a hot 1:1 mixture of cyclohexanone and methylethylcetone. This solvent mixture presented a better dissolution of PVC resin and of the dyeing. The combination of pH indicator was added to the PVC-cyclohexanone-methylethylcetone solution. The pH of the obtained solution was controlled by addition of trilaurylamine drops.

The obtained ink was applied with a 40 μm bar coater over a non absorbent paper. After the solvent evaporation, the coated paper can be cut in different shapes and sizes. The color change before and after irradiation depends on the PVC solution formulation and on the absorbed dose value.

RESULTS AND DISCUSSION:

In the development of dose indicator films, several pH indicator combinations together with some solvent solutions were tested and four formulations that presented the better results are here below showed and discussed.

Compound	Quantity
PVC resin	5,00 g
Methyl Yellow	0,12 g
Bromocresol Green	0,04 g
Methylethylcetone	35 ml
Cyclohexanone	35 ml
Trilaurylamine	5 drops

Table 1- Components of Formulation 1

Compound	Quantity
PVC resin	5,00 g
Methyl Yellow	0,08 g
Bromocresol Green	0,04 g
Methylethylcetone	35 ml
Cyclohexanone	35 ml
Trilaurylamine	5 drops

Table 2- Components of Formulation 2

Compounds	Quantity
PVC resin	5,00g
Methyl Yellow	0,10g
Bromophenol Blue	0,04g
Methylethylcetone	35ml
Cyclohexanone	35ml
Trilaurylamine	5 drops
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Table 3- Components of formulation 3

Compound	Quantity
PVC resin	5,00 g
Orange IV	0,04 g
Methyl Yellow	0,08 g
Bromophenol Blue	0,04 g
Methylethylcetone	35 ml
Cyclohexanone	35 ml
Trilaurylamine	5 drops

Table 4- Components of Formulation 4

The results obtained with the formulation 1 is presented in Table 5.

Color	Dark Green	Dark Green	Green	Yellow	Orange	Dark Red
Dose	0kGy	10kGy	20kGy	30kGy	40kGy	50kGy

Table 5 - Results shown by Formulation 1 after irradiation with electron beam.

In this case, the color of the indicator film changed from very dark green color (before the irradiation) up to dark and bright red (with 50 kGy absorbed dose value). But, it is not possible to notice very well, the color change in the range from 0kGy up to 20kGy, that is a very important dose range, in the most radiation processing. In the other hand, this formulation presented a very little fading, 8 months after the irradiation.

The table 6 shows the results obtained from the Formulation 2. This formulation tested a different pH indicator concentration. (Table 2).

Color	Dark Green	Green	Green-Yellow	Yellow	Dark Yellow	Orange	Dark Red
Dose	0kGy	10kGY	15kGy	20kGy	25kGy	30kGy	40-70kGy

Table 6- Influence of the variation in the concentration of pH indicators in the obtained results.

Table 6 shows that a small modification on the concentration of the Bromocresol Green indicator can modify the spectrum of the color obtained after the irradiation. This formulation presented a small color modification after the irradiation.

The table 7 presents the results obtained with the variation of one of the pH indicator components used. (Formulation 3).

Color	Dark Brown	Dark Brown	Green	Green-Red	Green-Red	Clear Brown	Dark Red	Red-Wine
Dose	0kGy	10kGy	15kGy	20kGy	25kGy	35kGy	40kGy	45-70kGy

Table 7- Variation of one of the pH indicator components used.

These films showed a deep color change by the addition of the Bromophenol Blue in the place of the Bromocresol Green indicator.

In the table 8, it is possible to observe the results shown by the Formulation 4 where, occurred the addition of three different pH indicators.

The continuous variation of the colors presented by formulation 4 is similar to that presented by formulation 3. This fact indicates that the addition of Orange IV only presents a small shift in the color spectrum. The

Color	Dark Brown	Dark Brown	Dark Brown	Clear Brown	Red	Dark Red	Dark Red	Bright Wine
Dose	0kGy	10kGy	15kGy	20kGy	25kGy	30kGy	35kGy	40-70kGy

Table 8- Addition of three pH indicators.

films began to show a color change after 20 kGy. The color changed from dark brown (before the irradiation) to bright wine, as it can be observed in Table 8.

4 - CONCLUSION

PVC resin is a polymer that presents some problems in its dissolution. The methylethylcetone is a recommended solvent for PVC but, in this preparation, it can not be used alone, due to its low boiling point. For this reason, the obtained ink presents a high variation in viscosity causing difficulties when applied over the paper. So, the choice of solvents is very important in these formulations. Several kinds of solvent combinations were tested, using always the methylethylcetone as a basic solvent. The 1:1 proportion of cyclohexanone and methylcetone showed the best results. The resulted ink is easy to be applied over the paper and the dry film presents good brightness and regular thickness.

The choice of a pH indicator combination is also important once it can cause a more visible change of color in a same dose range. Analyzing the obtained results in these studied formulations, it is possible to conclude that Methyl Yellow combined with Bromocresol Green offers the best continuous color change.

In the formulations here presented, the quantity of trilaurylamine used was similar to all studied cases in order to permit a better comparison but, the modification of the trilaurylamine concentration provides a shift in the color spectrum.

The variation of the dose rate in the electron beam accelerator does not modify the color spectrum obtained but, when these films are irradiated in panoramic ^{60}Co, where the maximum dose rate is about 5 times lower than those used in the electron beam accelerator, the color variation presented is different. The intermediate colors such as yellow and green-yellow. are not showed.

5- References

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