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STUDIES IN CROSS-LINKING PVC FOOTWEAR SOLING COMPOUNDS USING GAMMA-IRRADIATION

by :

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BACKGROUND

Irradiation cross-linking of polymeric materials has been known for some time but it is only in recent years that it has been put to commercial advantage. Well known uses are the modification of PVC for high temperature applications such as under-bonnet wiring, stove wiring, post office telecommunication wire and shrink tubing.

In South Africa interest in developing commercial applications for cross-linkable polymeric materials was initially stimulated through the work of the Atomic Energy Board at Pelindaba in late 1971 using a cobalt - 60 gamma radiation unit.

In conjunction with my Company, fundamental studies were carried out on, amongst other materials, plasticised PVC compounds for use in cable applications. The results of this work encouraged me to explore the potential offered by cross-linkable PVC for applications in less obvious areas such as flooring and footwear soling. The commissioning of the ISOSTER commercial facility in 1981, the largest of its kind in the world at the time, with a capacity of 6.million curies of cobalt-60, provided the opportunity to further this work.

Before discussing this work, I would like to say a few words on the process and some of the benefits conferred by it.

Irradiation of plastics has two main areas of interest, namely, in the sterilisation of medical products manufactured from plastic materials and, secondly, in changing the physical and chemical properties of a plastic material in such a way as to allow its use in applications where the unmodified material cannot be used. Irradiation of a plastic material results in cross-linking of the polymer 'molecular' chains and is somewhat akin to the vulcanising of rubber in the sense that it produces a product with improved resistance to heat, abrasion, cut-growth and chemical attack. Both gamma and electron beam irradiation processing may be used for the cross-linking. I do not propose to discuss the relative merits of each method except to say that gamma irradiation was chosen for this work mainly because of convenience (the ISOSTER unit being physically ready) and the enthusiasm of the ISOSTER staff. (Figs I-II).

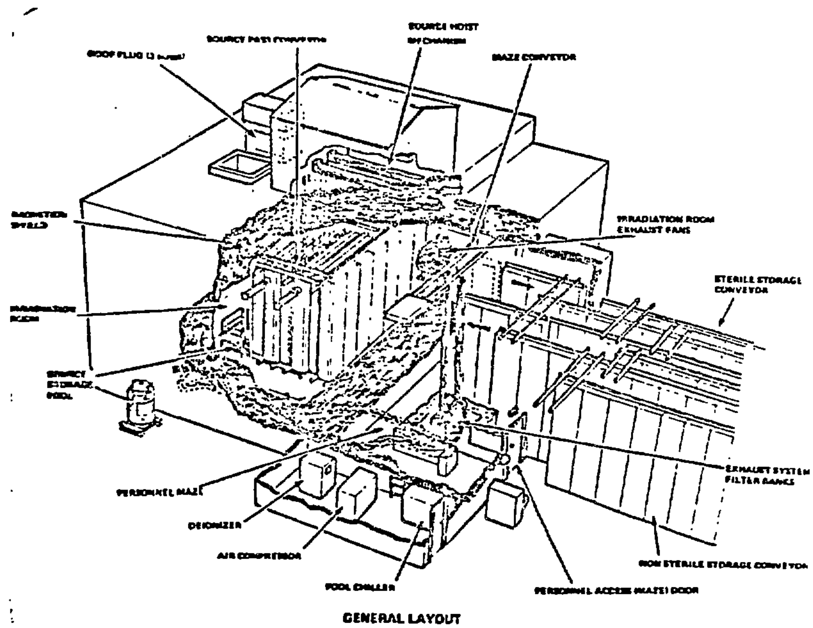

FIG. I - <u>GENERAL LAYOUT OF THE ISOSTER PLANT</u>

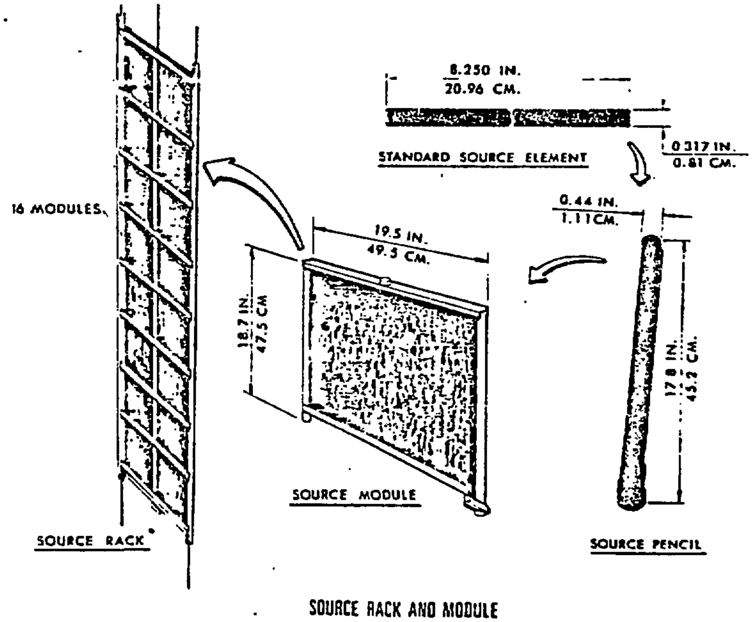

FIG II - <u>SAFETY FEATURES OF THE PLANT</u>

THE IRRADIATION X-LINKING OF PVC

A few brief words on the cross-linking of PVC are required in order to understand the potential scope and limitations as far as applications are concerned. Unlike polyethylene, PVC needs 'assistance' in that the irradiation energy required for cross-linking is greater and thus, as a consequence, can be very harmful to the PVC itself. It is therefore necessary to include a cross-linkable monomer which is typically an alkyl acrylate such as trimethylol propane trimethacrylate (TMPT). Very simply, although the mechanism is not fully understood, the cross-linking monomer, under irradiation, polymerises and forms a 'network' which restricts the movement of the PVC polymer chains. This acrylate monomer cross-links with both the PVC polymer 'chains' and the plasticiser present. The degree of cross-linking, measured in terms of the so called gel content, is determined by the level of the irradiation dose and the amount of cross-linkable monomer present. Care has to be taken to avoid over-dosage as polymer chain scission will take place, resulting in degradation and an end-product which is brittle and of little use. (Figs III and IV).

Earlier work has shown that, although properties such as tensile strength, elongation at break and electrical properties after irradiation are influenced by the type of plasticiser used, the gel content is for all practical purposes not significantly affected by the nature of the plasticiser. It is the gel content which determines to what extent the material is resistant to heat, and cut-growth for example. Clearly, therefore, the irradiation dosage, and cross-linkable monomer level are optimised to meet the requirements, taking care to limit the gamma irradiation dosage.

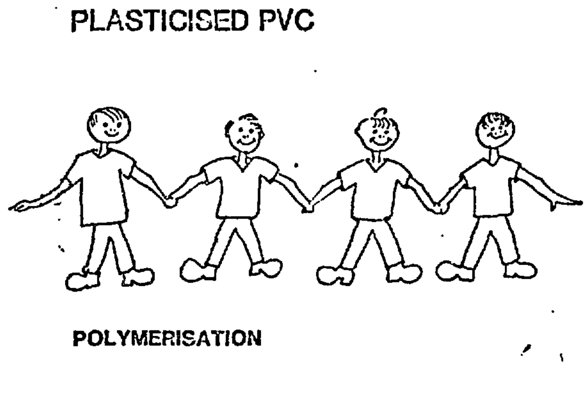

FIG III - A PICTORIAL ILLUSTRATION OF PVC POLYMERISATION

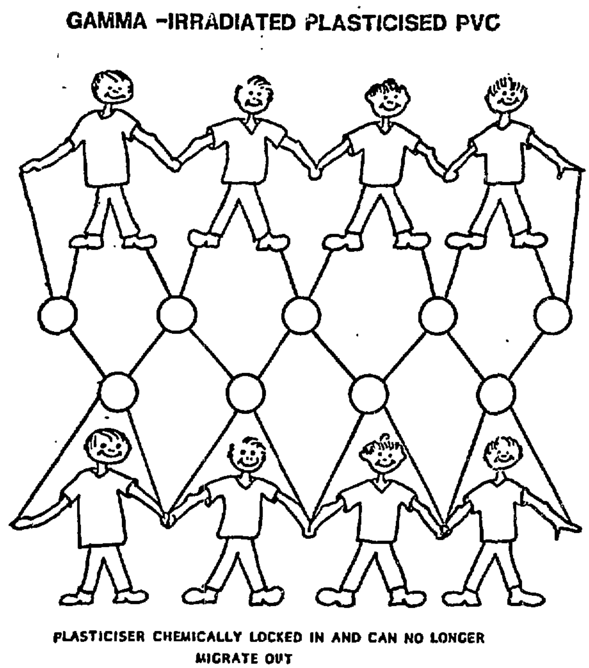

FIG IV - A PICTORIAL ILLUSTRATION OF GAMMA IRRADIATION OF PLASTICISED PVC

WHY PVC FOOTWEAR?

Earlier work on PVC cable compounds had already established the guidelines relating to dosage level, monomer concentration and plasticiser influence. My initial interest was the successful commercial application of PVC injection moulded flooring where it was possible to improve the abrasion resistance, dimensional stability and resistance to cigarette burns through cross-linking the PVC compound. PVC as a footwear soling material is well known and is now finding increasing use in industrial applications. However, there are areas which require superior resistance to heat, excessive abrasion and chemical attack. So far it has not been possible to meet these requirements with either standard PVC grades or modifications of them incorporating rubber. Examples of these demanding areas are steel works, the sweet industry and abattoirs. Having had some success with injection moulded floor tiles I was sufficiently encouraged to press ahead with the development of a X-linked PVC soling material for evaluation in these more stringent applications.

EXPERIMENTAL WORK AND RESULTS

One of the results of cross-linking is that the product hardens and, as far as footwear soling is concerned, can lead to wearer discomfort and premature flex cracking. This therefore imposes a practical limit on the extent to which the cross-linking process can be taken and also as a consequence, on the achievable degree of resistance to heat, cut growth and chemical attack. Standard PVC soling for industrial applications typically has a BS Softness of 80 (Shore A Hardness 57) and is usually formulated to include a polymeric plasticiser and/or a nitrile rubber to give improved abrasion resistance and resistance to plasticiser extraction by oils. It has also been established through experience that with thick soling, such as industrial footwear a BS Softness of 60 (Shore A Hardness 66) is the practical lower limit to ensure adequate serviceability. (Fig V).

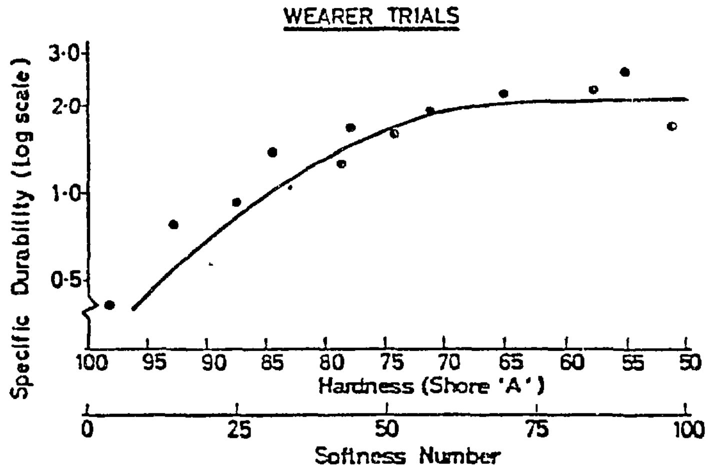

FIG V - SPECIFIC DURABILITY VERSUS BS SOFTNESS

Experimental investigations were thus aimed at maximising the gel content whilst ensuring that the softness after irradiation was not less than BS Softness 60.

The formulations which were studied are given below showing the physical properties before and after cross-linking. The compounds were made up in the usual way, i.e. Banbury compounded, milled and then injection moulded into unit soles for test purposes. The gamma irradiation dosage was varied to give the optimum gel content and also ensure that no degradation resulted. An optimum dosage level of 50 kGy and cross-linkable monomer level of 8 phr gave the desired overall properties.

FIG VI - TYPICAL CROSS-LINKING SOLING COMPOSITION

PVC RESIN (K-VALUE 65)	-	100	PARTS BY WEIGHT
* PLASTICISER (PHTHALATE)	-	70-90	PARTS BY WEIGHT
NITRILE RUBBER	-	25-35	PARTS BY WEIGHT
ESO	-	3-6	PARTS BY WEIGHT
HEAT STABILISER	-	3-6	PARTS BY WEIGHT
LUBRICANT	-	1-2	PARTS BY WEIGHT
CROSS-LINKING AGENT	-	5-12	PARTS BY WEIGHT

* Trimellitate used if article is to be exposed to high temperatures continuously.

	VULCANISED RUBBER SOLING	'WELVIC' I9/J130	'WELVIC' I9/J130 PLUS CROSS LINKING AGENT	'WELVIC' I9/J130 AFTER GAMMA IRRADIATION
BS SOFTNESS	40-60	90	92	60
SHORE A	77-66	53	53	66
RELATIVE DENSITY	1,24-1,29	1,17	1,16	1,16
MINERAL OIL CONTACT (24 hours)	SWELLS	SLIGHT SOFTENING	SLIGHT SOFTENING	NO CHANGE
IMMERSED IN PETROL (3 hours)	SWELLS	HARDENS AND CRACKS	HARDENS AND CRACKS	SLIGHT HARDENING
IMMERSED IN WEAK ACIDS (24 hours)	NO CHANGE	NO CHANGE	NO CHANGE	NO CHANGE
ABRASION	GOOD +	GOOD	GOOD	GOOD +
FLEXING	NO CHANGE	SLIGHT CHANGE	SLIGHT CHANGE	NO CHANGE
IN CONTACT WITH HOT METAL (130 °C)	SCORCHES	MELTS AND SPREADS	MELTS AND SPREADS	SCORCHES
SOFTENING TEMPERATURE (°C)	WELL ABOVE 120 °C (SCORCHES)	70	70	120
MOULDABILITY	FAIR	GOOD	GOOD	GOOD
INJECTION CYCLE (Seconds) (Average mens industrial sole)	60-120	8	8	8
USE OF SCRAP	NIL	YES	YES	NIL
COLOURS	LIMITED	ALL	ALL	ALL

FIG VII - PHYSICAL PROPERTIES BEFORE AND AFTER GAMMA IRRADIATION

INFLUENCE OF CROSS-LINKING ON PHYSICAL PROPERTIES OF AN INDUSTRIAL SHOE SOLING COMPOUND

- IMPROVED HEAT RESISTANCE
- IMPROVED CUT GROWTH RESISTANCE
- IMPROVED ABRASION RESISTANCE
- IMPROVED ADHESION IN THE DMS PROCESS (DIRECT MOULDED SOLE)
- GREATLY REDUCED PLASTICISER AND ADDITIVE MIGRATION
- NO PROCESSING PROBLEMS ON CONVENTIONAL INJECTION MOULDING EQUIPMENT

FIG VIII - INFLUENCE OF CROSS-LINKING ON PHYSICAL PROPERTIES OF AN INDUSTRIAL SHOE SOLING COMPOUND

In the course of the studies it was found that, unlike plasticiser, the nitrile rubber present influenced the gel content obtainable. The maximum gel content was obtained with 30 phr of nitrile rubber.

GEL CONTENT VERSUS % NITRILE RUBBER IN COMPOUND

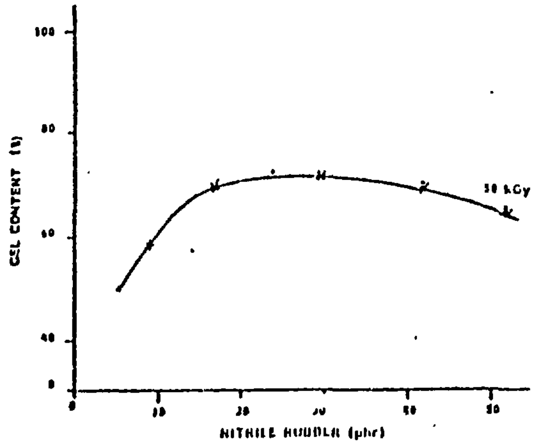

FIG IX - GEL CONTENT VERSUS % NITRILE RUBBER IN COMPOUND

POWDERED NITRILE RUBBER (phr)	0	5	8	10
DOSE 25 kGy	22,5	30,2	32,6	45,0
DOSE 50 kGy	32,7	37,6	35,3	56,6

FIG X - GEL DATA WITH RESPECT TO FORMULATION VARIATION OF AN INDUSTRIAL SOLING COMPOUND CONTAINING 8 PHR OF TRIMETHYLOL PROPANE TRIMETHACRYLATE

	BS SOFTNESS	SHORE A HARDNESS	% WEIGHT LOSS (7 days at 22 °C) MOTOR OIL	ISO-OCTANE
BEFORE GAMMA IRRADIATION	80	57	-12	-35
AFTER GAMMA IRRADIATION	60	66	-2,5	-0,7

FIG XI - INDUSTRIAL SOLING - DEGREE OF GEL AND ITS EFFECT IN MOTOR OIL AND ISO-OCTANE

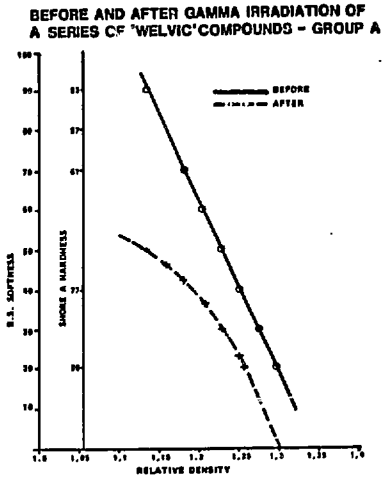

FIG XII - BEFORE AND AFTER GAMMA IRRADIATION OF A SERIES OF 'WELVIC' COMPOUNDS

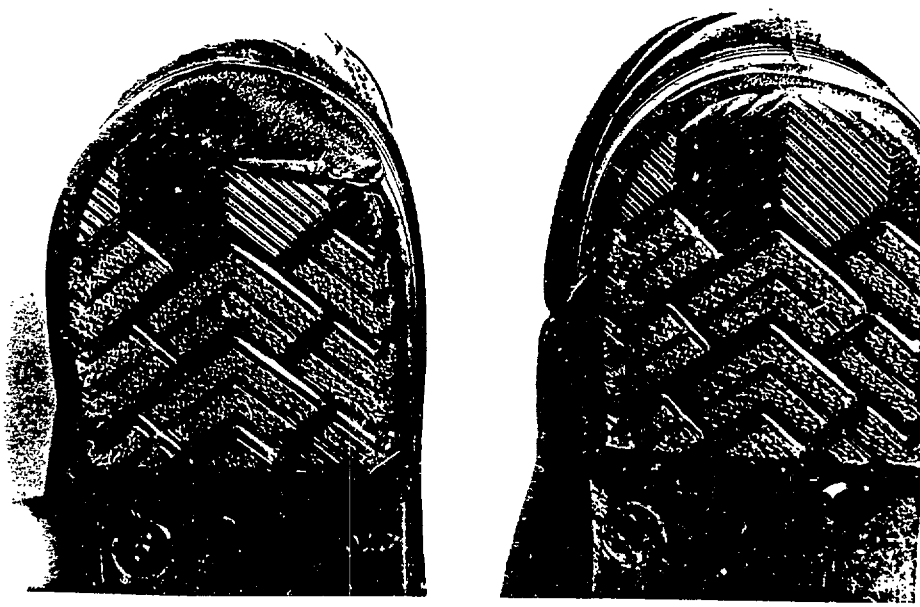

FIG XIII - AN INJECTION MOULDED PVC/NITRILE RUBBER SOLED BOOT BEING HELD ON A HOT PLATE SET AT 130 °C BEFORE AND AFTER GAMMA IRRADIATION

Having obtained a practical formulation with the desired softness after irradiation the next step was to test the product for its resistance to heat, chemical (solvent) attack and abrasion.

Wearer trials which have been in progress for two months are very encouraging.

FUTURE WORK

It is important to note that although the initial laboratory work has been encouraging the project is still of a speculative nature. Much needs to be done, particularly if a cost-effective production operation is to be achieved. Further studies will be dependent on the outcome of the current wearer trials. There is no doubt that the technology opens the door to a number of interesting applications. Apart from industrial footwear, several other projects which have interesting possibilities are under evaluation. Examples are gumboots, the replacement of steel toe-caps, shoe shanks, flow moulded uppers, and a conducting PVC battery terminal clip. Hopefully these will come to fruition and add to the growing number of applications in which cross-linked PVC can be utilised.

In conclusion, the work so far undertaken indicates the possibilities that are open for this technology with particular reference to plasticised PVC compounds. My old chief at ICI Plastics Division in England, the late Dr John Haslam, used to remind me that "The Theory Guides - The Experiment Decides". This slogan certainly applies to the technology of gamma irradiation of plasticised PVC.

Quotation by the late

Dr JOHN HASLAM, D. Sc.

(Chief Chemist of ICI Plastics Division)

'THE THEORY GUIDES,

THE EXPERIMENT DECIDES'

FIG XIV - THE THEORY GUIDES - THE EXPERIMENT DECIDES

I would like to thank the Directors of AECI for permission to present this paper. I would also like to acknowledge the assistance given to me by Dr Andy Roediger of ISOSTER, and also the Calan Group and Codesta Plastics for their co-operation in allowing trials to be undertaken on their equipment. Thanks are also due to Mr S Hefer of the SABS for discussions on gamma-irradiated polymers and allied products and to Dr Guy Mears of AECI for his valuable guidance in the preparation of this paper.

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