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EVALUATION OF KEROCIL—A CHLORINATED MINERAL OIL AS PRIMARY PLASTICIZER

SHABBIR AHMED QURESHI, A.H.K. YOUSUFZAI and SHABIH-UL-HASSAN

P.C.S.I.R. Laboratories, Karachi 39

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Kerocil[1] a name given to a chlorinated mineral oil (C_{12}-C_{17}) has been found to be a good primary plasticizer for polyvinyl chloride (PVC). The process of its manufacture together with a detailed study of its plasticising properties on polyvinyl chloride has been carried out. The results of this study compare favourably with the other well-known primary plasticizer namely the dioctyl phthalate (DOP).

Plasticizers as the name implies introduce the various plasticizing properties namely the flow-flexibility, elastic modulus and the melt viscosity in the resins. The plasticized resins find their application in shoe, clothings, water-proof materials, artificial leather, toys and numerous other industries. At present its major use is with the PVC as a plasticizing agent.

In 1870, Job and Hyatt[2] were the first to discover that camphor could plasticize nitrocellulose. Later the introduction of triphenyl phosphate in 1912 followed by tricresyl phosphate did help to alleviate the situation. During and after the World War II, the rapidly growing vinyl industry has come out to be the largest consumer of the plasticizers.

Plasticizers have been generally classified as the primary and the secondary plasticizers. Primary plasticizers are those which do not exude or spew from a plasticized composition after flexing or on long storage, under accelerated aging tests. Those which have limited compatibility are termed as secondary-plasticizers. Thus broadly speaking a primary plasticizer is completely compatable with resins, fillers, pigments and is sufficiently permanent i.e. it retains the "plasticizing quality" throughout its useful life. It is still difficult to classify a plasticizer, some may be called primary while the other a secondary e.g. Di-isodecyl phthalate is primary for PVC and secondary for PVA, thus showing that there is no hard and fast rule to demarcate one from the other.

A plasticizer in the form of chlorinated hydrocarbons based on the indigenous raw materials namely the petroleum hydrocarbons and the chlorine gas has been prepared in these laboratories. The plasticizer, which has been patented under the name of Kerocil, compares favourably with the imported plasticizer as shown in the present study.

Experimental

Production of Kerocil

Petroleum hydrocarbons (C_{12}–C_{17}) boiling in the range of 150–250°C, is cooled to 20°C in a vertical glass or glass-lined column fitted with cooling coils. Chlorine gas is injected at a rate varying between 0.2 to 1 lb/hr per litre of the hydrocarbons. The chlorination is continued till the density of the chlorinated hydrocarbons rises to 1.20–1.25 g/cc.

The resulting chlorinated hydrocarbons is scrubbed free of the acid and dried over anhydrous, sodium-sulphate.

Physical Testing of Kerocil[3]

Experiments were carried out on casted PVC sheets using DOP and Kerocils (hereafter denoted as Kerocil-I and II) Kerocil I has the density of 1.25 and chlorine chntents 45% while Kerocil II has the density of 1.3 and chlorine contents of 50–60%.) as plasticizers, with the following compositions: PVC 100 parts; Plasticizer 80 parts; Fillers 15 parts; Pigment 1 part; Stabilizer 1 part.

The ingredients were throughly mixed and left for 24 hr. The casted sheets were cured at 165°C and tested for hardness, tensile strength, effect of solvents and the volatility.

(*a*) *Compatability Test.*—Compatability as Boyen[4] views it, is the determined quantity of the plasticizer that can be added to polymer before phase separation occurs.

It has been found that the Kerocils are compatable with PVC upto 50% without exudation.

(*b*) *Shore Hardness Tests.*—Plasticized sheets are normally low in hardness. The hardness of the

casted sheets were tested according to ASTM recommended methods,[5] using the Shore durometer. The values obtained are DOP 46, Kerocil I 45–46, and Kerocil II 55–56.

These results are in agreement with those obtained from the DOP plasticized sheets under identical conditions.

(*c*) *Tensile Strength and Percent Elongation.*—The tensile strength and the percent elongation were calculated by the recommended ASTM methods and are given in Table 1.

TABLE 1.—TENSILE STRENGTH AND ELONGATION% AS FUNCTION OF THE PLASTICIZER.

PVC plasticized with	Tensile strength lb/m²	Percent elongation
DOP	1665	293
Kerocil I	1992	287.5
Kerocil II	1695	393.5
Kerocil I 50 parts DOP 50 parts	1506	237.5
Kerocil II 50 parts DOP 50 parts	1578	256.2

The results as shown are satisfactory for both types of the chlorinated paraffins, i.e. Kerocil I and II.

(*d*) *Effects of Solvents on Plasticized Sheets.*—The plasticized casted sheets were kept in number of common solvents in order to assess its serviceable life and aging properties. The results (Table 2) indicate that the gain in weight in Kerocil plasticised sheets is minimum in water which means that the Kerocil as plasticizer imparts maximum waterproofing quality to the plasticized sheets from the PVC. In organic solvents and soap solution, the lossess compare favourably with Mesimol, another well-known imported plasticizer (see Table 2).

TABLE 2.—COMPARATIVE WEIGHT LOSS IN DIFFERENT SOLVENTS.

Plasticizers used	Gain in wt in water %	Loss in Ethyl alcohol %	Loss in Cotton seed oil %	Loss in Soap solution %
DOP	1.0	29	14	0.2
Kerocil I	0.5	6	12	2.0
Kerocil II	1.0	6.5	20	2.0
Mesimol	2.8	3.5	9.0	2.0

(*e*) *Volatility.*—The sheets casted from PVC with DOP, Kerocil I, Kerocil II and Mesimol were kept at 60°C (±1°C) for 80 hr the percentage loss in weight is shown in Table 3. This method is recommended by Reed and Conner.[6]

TABLE 3.—PERCENT LOSS AS FUNCTION OF TEMPERATURE.

Samples	% Loss
Kerocil I	2.02
Kerocil II	3.06
Mesimol	2.5
DOP	1.8

Discussion

Chlorinated paraffins have been used as secondary plasticizers but the present study shows that the paraffins (C_{12}–C_{17}) having a boiling range of about 150–300°C, (commonly known as kerosine oil) when chlorinated can also be used as a plasticizer. The chlorinated product having chlorine content of about 50–55% and a density range of 1.25–1.30 has proved to be most satisfactory as a primary plasticizer, as indicated by the results according to the recommended methods of testing in ASTM and BSS. The results compare favourably well with the other plasticizer namely the DOP, Mesimol, etc.

The Kerocil also possess better water repellant properties.

During aging tests, it has been found that a dark brown colour is developed after long storage but this does not alter the properties of the plasticizer.

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