

## Activation of Plastic Surfaces in a Plasmajet

Russell M. Mantell and William L. Ormand

AeroChem Research Laboratories, Inc.  
Princeton, New Jersey

### INTRODUCTION

The surface of a polymer such as polyethylene is difficult to paint, print, dye or laminate, unless previously prepared.<sup>1</sup> Methods of activating polymer surfaces may be conveniently divided into chemical, thermal, corona discharge, and the described non-equilibrium plasmajet types.

Typical chemical methods employ chromic acid solutions<sup>2</sup> or a combination of ozone and hydrogen halide.<sup>3</sup> They do not appear to be of commercial importance.

Thermal methods which have been utilized industrially impinge heated air upon the surface<sup>4</sup> while cooling the bulk of the plastic. The air is either preheated<sup>4</sup> or a direct flame<sup>5</sup> may be played on the surface.

Corona discharge methods, of recent industrial importance, pass polyethylene film over a rotating drum electrode while discharging a high frequency alternating current to the drum through a small air gap from a knife-edge electrode.<sup>6</sup> Disadvantages of this process include puncturing of the polymer, inapplicability to inert, polar or readily-degraded polymers, and difficulties encountered in the treatment of irregularly-shaped or partly-conducting objects.

All of the above methods appear to involve some form of oxidation of the surface polymer while minimizing degradation of the bulk polymer. It is a convenient oversimplification to assume the thermal methods utilize diatomic oxygen, the corona discharge methods utilize triatomic oxygen, and a nonequilibrium

plasmajet method would utilize monoatomic oxygen. The latter was presumed to be the most reactive of the three oxygen species at low temperatures. Therefore, the oxygen plasmajet process was investigated in the hope of obtaining a novel,<sup>8</sup> rapid and economical process for surface treatment capable of application to a variety of polymer surfaces.

The proposed plasmajet process described below utilizes a stream of oxygen which is partially dissociated by a glow discharge, expanded at high velocity through an orifice into a region of lower pressure, and then impinged upon the surface.

### EXPERIMENTAL

Apparatus. The nonequilibrium plasmajet equipment utilized for the research is described elsewhere.<sup>9,10</sup> It was modified by insertion, 12 inches downstream from the nozzle electrode, of a quick-opening Pyrex port of 4 inch I.D. by 12 inch length (measured at 90° from the axial reactor center). The port was closed by a 3/4 inch thick "Lucite" sheet, centrally drilled and tapped for a brass sleeve through which was loosely fitted a 1/4 inch diameter metal rod terminating in a 3 inch diameter by 1/4 inch thick brass target. The target was mounted so that the gas flow was parallel to the sample surface. Covering the target was a detachable metal hood into which the target and sample fit snugly to prevent exposure while operating conditions were being established. A thin Teflon sheet, cemented within the hood, contacted the plastic surface to be treated, to minimize abrasion. The hood and target arrangement was such that the specimen could be exposed at any desired distance from the jet axis. Vacuum-tight sliding seals were obtained by means of lubricated rubber couplings. The port permitted removal of the target and specimen within seconds after specimen exposure to permit an estimation by the use of a surface thermocouple of the film temperature attained. Insertion of the port into the apparatus was possible at various distances downstream from the nozzle electrode. Provisions were made for operation of the apparatus in a darkened room in order to permit visual observation of afterglow phenomena.

Materials. Oxygen, extra dry grade, and helium, 99.99% purity, were obtained in cylinders from the Matheson Company and dried immediately before entrance into the reactor by passage over activated alumina.

The following polymer samples were supplied through the kindness of the manufacturers: polypropylene, pro-fax type 6420 (Hercules); polyethylene, hi-fax type 1625 (Hercules); polyester, Mylar (duPont); polytetrafluoroethylene, Teflon type T.F.E. (duPont); polytrifluorochloroethylene, Kel-F type KX 8202 (3M Corp.); and polyvinyl fluoride, Tedlar type 50-SG20 TR (duPont).

The printing ink, Excellobrite White 500 (Sun Chemical Corp.) was similarly obtained. The lacquer employed was Duragloss, Camelia (A. R. Winarick, Inc.); the India Ink used was Pelikan Waterproof Drawing Ink (Gunther Wagner Co.) and the pressure-sensitive resin was "Scotch" Brand 600 acetate tape (3M Corp.)

Weightings. To remove electrostatic charges, a sample of the desired film, 1.0 mil thickness by 3.0 inches in diameter, was placed on the target, hooded and subjected to a 200 to 300 watt discharge at a pressure of about 1.0 Torr for a period of one second. The specimen was immediately weighed to 1/10 mg. on an analytical balance, replaced in the apparatus, exposed to the partially dissociated oxygen stream, reweighed and stored in air-tight containers. Finger cots and forceps were used in handling the specimens at all times.

Scratch Test. Exposed and control specimens of film were painted with commercial printing ink, lacquer and drawing ink, air-dried for at least 24 hours at room temperature, and manually scratched with a pointed stylus. Ratings were 1, 2 or 3 on a scale corresponding to unimproved, improved or greatly improved resistance to scratch removal relative to the control specimen.

Peel Strength Test. Exposed and control specimens of film were cut to 1/2 inch width and welded to pressure-sensitive tape of equal width. The weld was peeled apart at one end of the laminate. From the peeled end, the polymer was secured to a fixed point and the pressure-sensitive tape was attached to a balance pan, the weld itself being perpendicular to the force to be applied. The minimum force, in grams per inch, necessary to peel apart the remainder of the weld<sup>11</sup> was obtained by a successive increase of weights on the balance pan.

Surface Wetting Test. Exposed and control film specimens were secured to a horizontal table. A drop of water of 0.05 ml. volume was placed upon the film and the table slowly raised toward the vertical by a gear arrangement until the drop began to move across the surface. The angle which the film surface then made

with the horizontal is a measure of its surface wetting by water<sup>12</sup> and has been related to the adhesive properties of the film.<sup>13</sup>

Conditions. Unless otherwise noted, the conditions employed were as follows: 6 inch discharge electrode gap, 5/16 inch nozzle orifice diameter, 1 mil by 3 inch diameter sample, downstream pressure 3 Torr, upstream pressure 6 Torr, oxygen flow  $5 \times 10^{-3}$  mol/sec, axial distance 12 inches from discharge nozzle, radial distance from stream axis to sample 0.75 inches, maximum film temperature 80°C, and exposure time 900 seconds. The discharged gas contained 3 to 4% oxygen atoms at these conditions, as determined by light titration techniques.<sup>14</sup>

## RESULTS

Reactor Parameters. A direct proportionality between weight loss and exposure time is shown in Figure 1 for polypropylene samples exposed under the conditions described earlier. The weight loss was also proportional to electric discharge power as shown in Figure 2. The intensity of the visually-observed afterglow<sup>14</sup> was in qualitative agreement with the observed variation of weight loss. This was also true for the variation in afterglow downstream. Figure 3 shows that the effect of the stream on sample weight loss decreased as one proceeded further downstream from the nozzle exit. As the sample was moved from the center of the exhaust stream outward, the weight loss decreased rapidly and then leveled off. The leveling off at the wall boundary is consistent with the observation that the glow downstream of the discharge exit filled the whole tube, of 1.5 inches in diameter. No significance should be placed on the fact that the sample weight loss within this region decayed and was not flat, because the large structure of the sample holder would have destroyed any local atom distribution across the stream.

In the absence of electrical discharge or when oxygen was replaced by helium, no significant weight changes in the sample were observed. No significant deviation in the transmission of infrared spectra of the treated and control samples, was resolvable on a Beckman IR5 Spectrophotometer.

The results for the weight change and the scratch, peel strength and surface wetting tests for polyethylene, polypropylene,

polyvinyl fluoride, polyethylene terephthalate, polytetrafluoroethylene, and polytrifluorochloroethylene films exposed to the oxygen plasmastream are shown in Table I.

A rather good correlation is observed between the weight loss for polymers, upon exposure, with the scratch test, which is a measure of the strength of the substrate bond with inks and lacquers. Correlation with the other two properties, however, is not so clear. In the peel strength test, it is interesting to note that polypropylene has a greater strength than polyethylene before treatment, and is not essentially affected, while for polyethylene, a large change -- about three -- is effected. However, the opposite result is experienced when comparing polyethylene and polypropylene for the surface wetting test, *i.e.*, polypropylene is more affected. The surface wetting is most effective for the polyester and then, surprisingly, there is a large effect for the polytrifluorochloroethylene. In general, one might conclude from this table that the less stable hydrocarbon polymers of ethylene and propylene are relatively reactive to the oxygen stream, while the perfluorocarbon and perfluorochlorocarbon polymers are virtually inert, except for surface wetting. An intermediate order of reactivity is shown by the moderately stable and polar polyvinyl fluoride and polyethylene terephthalate (polyester).

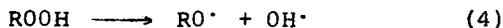
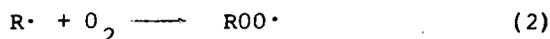
It is interesting to speculate on the effectiveness of the oxygen atoms in the stream for reacting with the surface. If we assume the oxygen atom reacts with a  $\text{CH}_2$  group, we can then calculate the effectiveness of the stream by computing the number of oxygen atoms striking a  $\text{CH}_2$  group on the surface. If we assume a surface cross-section for the  $\text{CH}_2$  group in polyethylene of  $25 \times 10^{16} \text{ cm}^2$ , from the number of oxygen atoms which strike the surface under the experimental conditions,  $6 \times 10^{19}$  per  $\text{cm}^2 \text{ sec}$ , and from the observed weight loss, assuming the  $\text{CH}_2$  group is removed from the surface,  $2 \times 10^{15}$   $\text{CH}_2$  groups per  $\text{cm}^2 \text{ sec}$ , will be removed. This means that about one in  $10^4$  oxygen atom collisions with the surface is effective. These numbers indicate that several monolayers of  $\text{CH}_2$  surface are removed per second, which is difficult to rationalize with the observation in Table I that surface properties change considerably from one to 900 seconds.

## DISCUSSION

Corona Discharge and Thermal Oxidations. Polyethylene film placed directly in a corona discharge of oxygen at one atmosphere has been shown to experience a loss in weight which is directly proportional to the time of exposure, and to gain weight when placed just below the discharge.<sup>15</sup> Cooper and Prober related the formation of oxygenated surface products to reactions of the ozone (formed in the discharge) with double bonds of unsaturated polyethylene molecules. They ascribed the loss in weight of the polymer placed directly in the discharge to other reactions involving either electron or atom attack on the polymers, their data being inconclusive for a choice of mechanisms.

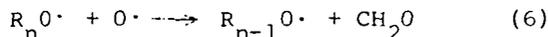
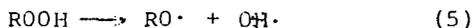
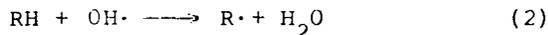
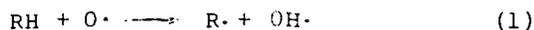
The present plasma work establishes that atom attack of the polymer is indeed a possible mechanism for surface reaction in the corona discharge although it does not rule out the possibility of other mechanisms.

Turning from corona discharge to thermally-induced oxidation of polyethylene and related compounds, the following simplified sequence of initial reactions has been discussed by Luongo<sup>16</sup> and Grassie<sup>17</sup>



Plasmajet Oxidations. The data presented in this paper can be accounted for by the assumption of reaction of oxygen atoms with polymer to form oxygenated macromolecules which ultimately, through chain scission reactions, form products of lower molecular weight and higher vapor pressure. These volatilize and continuously expose fresh polymer surface. At steady-state conditions, an appreciable concentration of oxygenated macromolecular species must remain on this "fresh" polypropylene surface. The relatively polar oxygenated sites introduced on the polymer are responsible for the change in the surface properties of the treated samples shown by the data for the scratch, peel strength and wetting tests in Table I.

A possible series of reactions for the surface oxidation of polymer in the oxygen plasmajet is given below:



The collision of an oxygen atom with polymer initiates reaction as shown in steps (1) and (2). These free radical steps are unlike thermal initiation, in which energy must be supplied to the polymer.<sup>17,18</sup> Steps (3) through (5), identical with the thermal sequence, show reactions of the undissociated oxygen (from the gas phase) with the surface polymer radicals. Degradation of polymer molecules by oxygen atoms is shown in step 6 to lead smaller radicals. These smaller radicals may sublime from the surface accounting for the weight loss. The surface recombination of polymer radicals is shown in step (7). Oxidation reactions may continue in the gas phase. Where chain termination steps such as (7) control the rate at which the polymer is degraded, the overall rate with respect to polymer consumption at a given free radical concentration can be expected to be constant with time in agreement with the data of Fig. 1.

#### COMMERCIAL CONSIDERATIONS

In corona discharge processes, the exact geometry and electrode separation as well as the composition and shape of the material treated can be expected to be of critical importance. Corona discharges concentrate at physical defects (pinholes, voids, and conductive occlusions) in polymers and rapidly enlarge them by electrical breakdown.<sup>7</sup> In the nonequilibrium plasmajet process, the isolation of the discharge from the material treated

will make these factors relatively unimportant. The technique described in the paper has been experimentally used to treat small cubes, cylinders, partly-metallized films, and even textiles of polypropylene. There was no observed alteration of the physical integrity of the objects.

Cost estimations show the proposed plasmajet process to be competitive with corona discharge processes for polymer surface activation.

#### SUMMARY

A nonequilibrium plasmajet process for activation of polymer surfaces has been developed. A stream of oxygen is partially dissociated by a glow discharge, expanded to high velocity through an orifice into a region of lower pressure and impinged on the desired surface. Parameters measured before and after treatment of a variety of polymers include weight, surface bonding characteristics, and wettability. The weight loss of the polymer increases with exposure time, discharge power, and proximity to the atom source. In general, there is a correlation between the weight loss and the surface properties.

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REFERENCES

1. Staff Article; Chem. & Eng. News 40, 30 (1962).
2. Horton, P.V.; U.S. 2,658,134 (1954).
3. Wolinski, L. E.; U.S. 2,715,075-6 (1955).
4. Kreidl, W. H. and Hartman, F.; *Plastics Tech.* 1, 31 (1955).
5. Kritchevar, M. F.; U.S. 2,648,097 (1957).
6. Traver, G. W.; B. P. 771,234 (1953).
7. Oliphant, Murray, Jr.; *Insulation* 9, 33 (1963).
8. Patent Applications on the process have been filed.
9. Rosner, L.E. and Calcote, H.F., AeroChem TM-10 October 1958; ASTIA AD 207 590.
10. Fontijn, A., Rosner D.E., Kurzius, S.C., *Can. J. Chem.* (submitted).
11. Wechsberg, L. E., and Webber, J.B.; *Soc. Plastics Eng. Tech. Papers* 5, 846 (1959).
12. McLaughlin, T.F.; *Soc. Plastics Eng. Tech. Papers* 6, 37 (1960).
13. Allan, A. J. G.; *J. Polymer Science* 38, 297 (1959).
14. Kaufman, F.; *Proc. Roy. Soc. A* 247, 123 (1958).
15. Cooper, Glenn D. & Prober, Maurice; *J. Polymer Science* 44, 397 (1960).
16. Luongo, J. P.; *J. Polymer Science* 42, 139 (1960).
17. Grassie, N.; Chemistry of High Polymer Degradation Processes, Butterworths Publications, Ltd., London, England (1956).

TABLE I

EFFECTS OF NONEQUILIBRIUM OXYGEN STREAM  
ON POLYMER SURFACE PROPERTIES

TEST	Scratch, Numerical Rating <sup>a</sup>	Peel Strength, grams/inch	Surface Wetting, degrees tilt	Weight Loss, mg/sample <sup>b</sup>
TIME, sec	1 900	0 1 900	0 1 900	900
Polyethylene	2.7 3.0	360 420 1000	35 38 51	3.8
Polypropylene	3.0 3.0	1400 1350 1300	16 52 42	3.7
Polyvinylfluoride	2.0 2.5	100 120 200	23 38 23	3.4
Polyester	1.2 2.1	200 290 520	41 13 12	1.1
Polytetrafluoro- ethylene	1.0 1.5	66 50 54	25 33 39	0
Polytrifluoro- chloroethylene	1.5 1.5	210 220 200	20 36 53	0

a. Ratings 1 - 3 correspond to no change to great change.

b. 7.06 in<sup>2</sup> of surface area per sample were used.

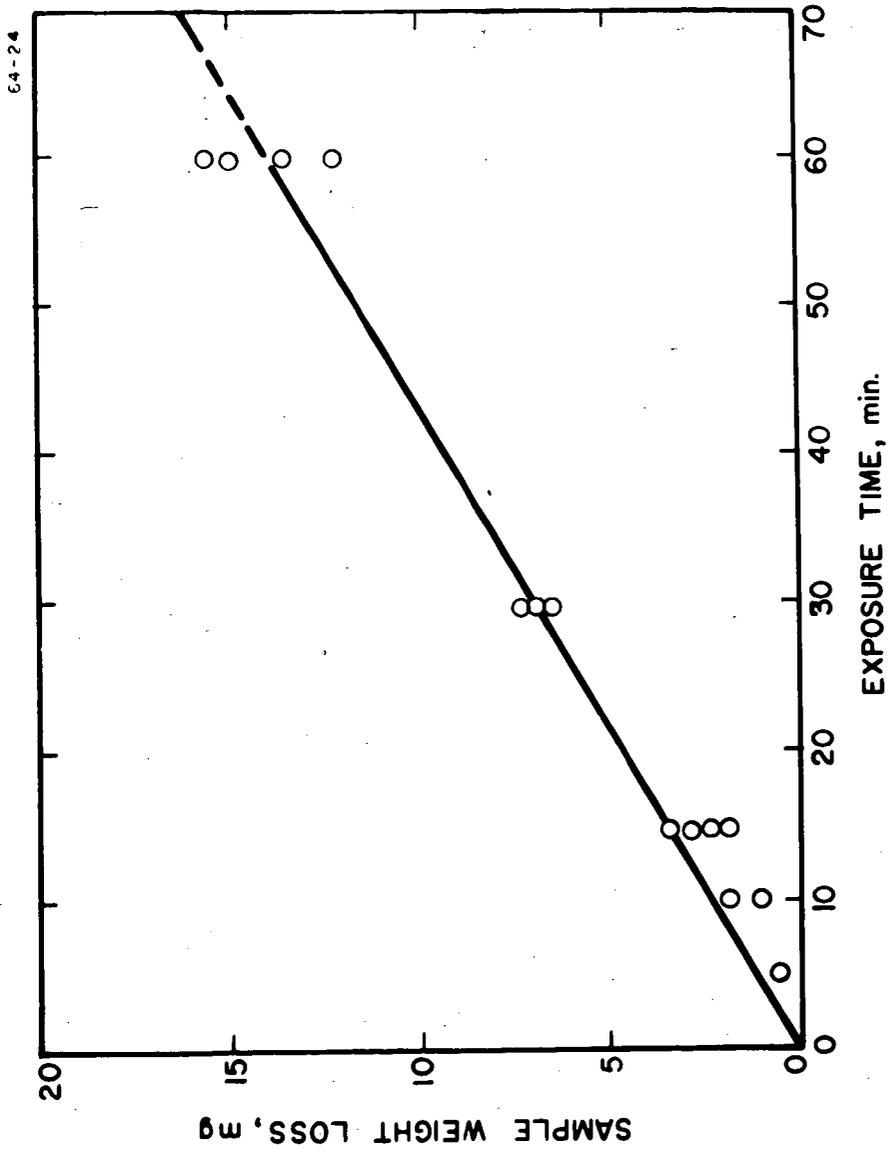


FIG. 1 THE INFLUENCE OF EXPOSURE TIME ON THE WEIGHT LOSS OF POLYPROPYLENE

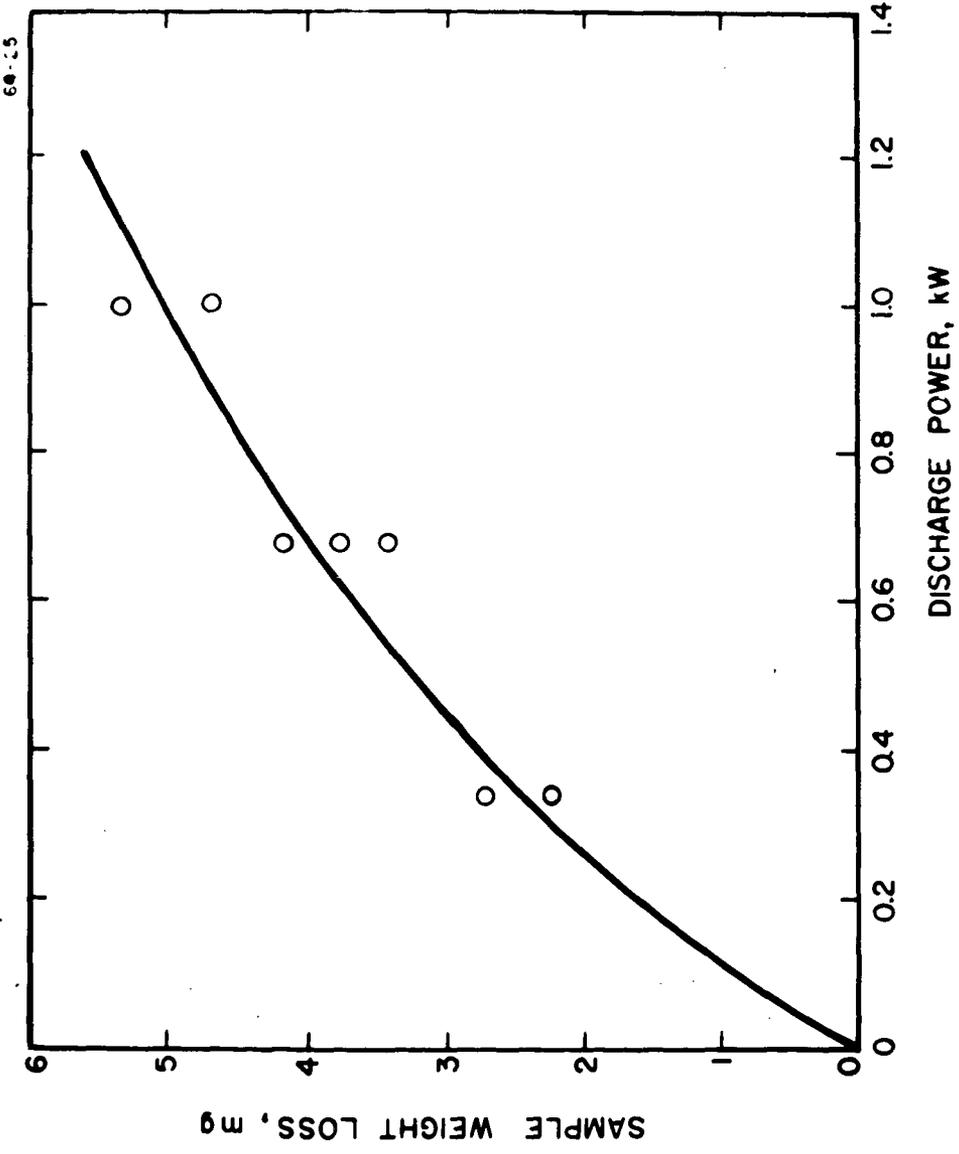


FIG. 2 THE INFLUENCE OF DISCHARGE ELECTRIC POWER ON THE WEIGHT LOSS OF POLYPROPYLENE

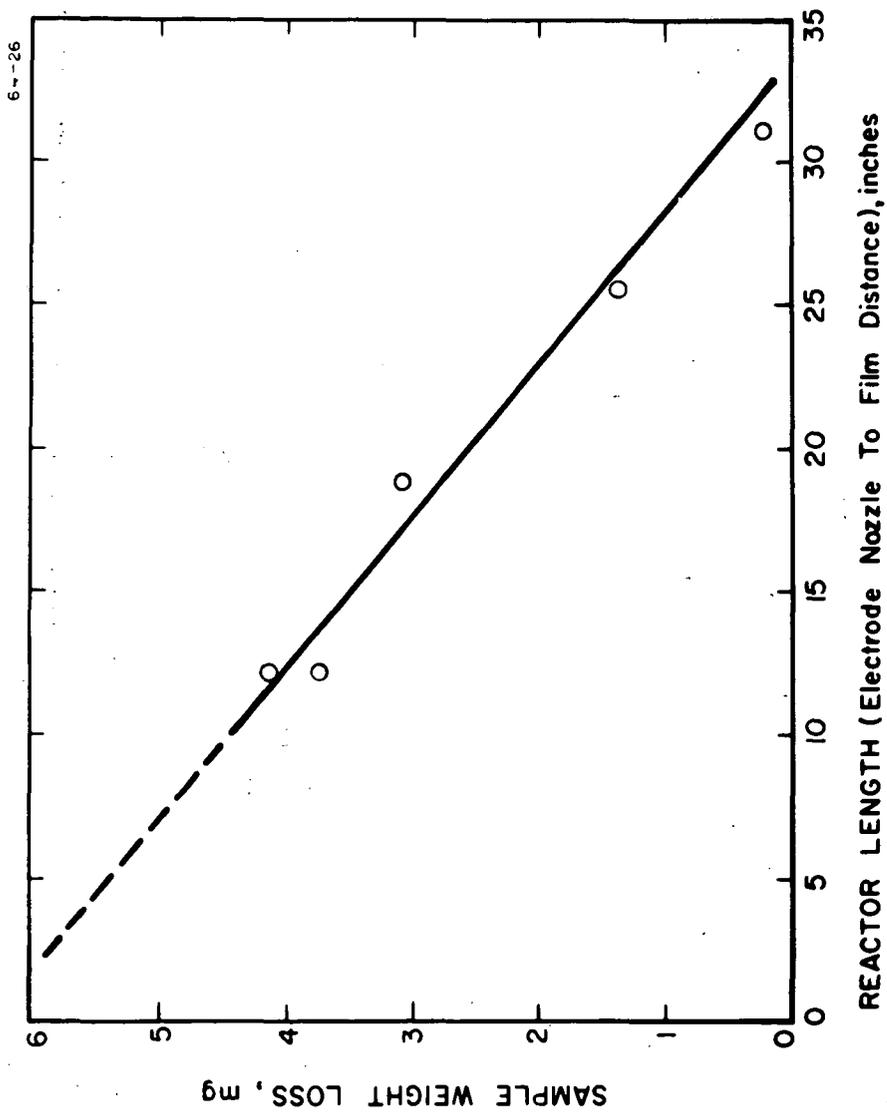


FIG. 3 THE INFLUENCE OF REACTOR LENGTH ON THE WEIGHT LOSS OF POLYPROPYLENE

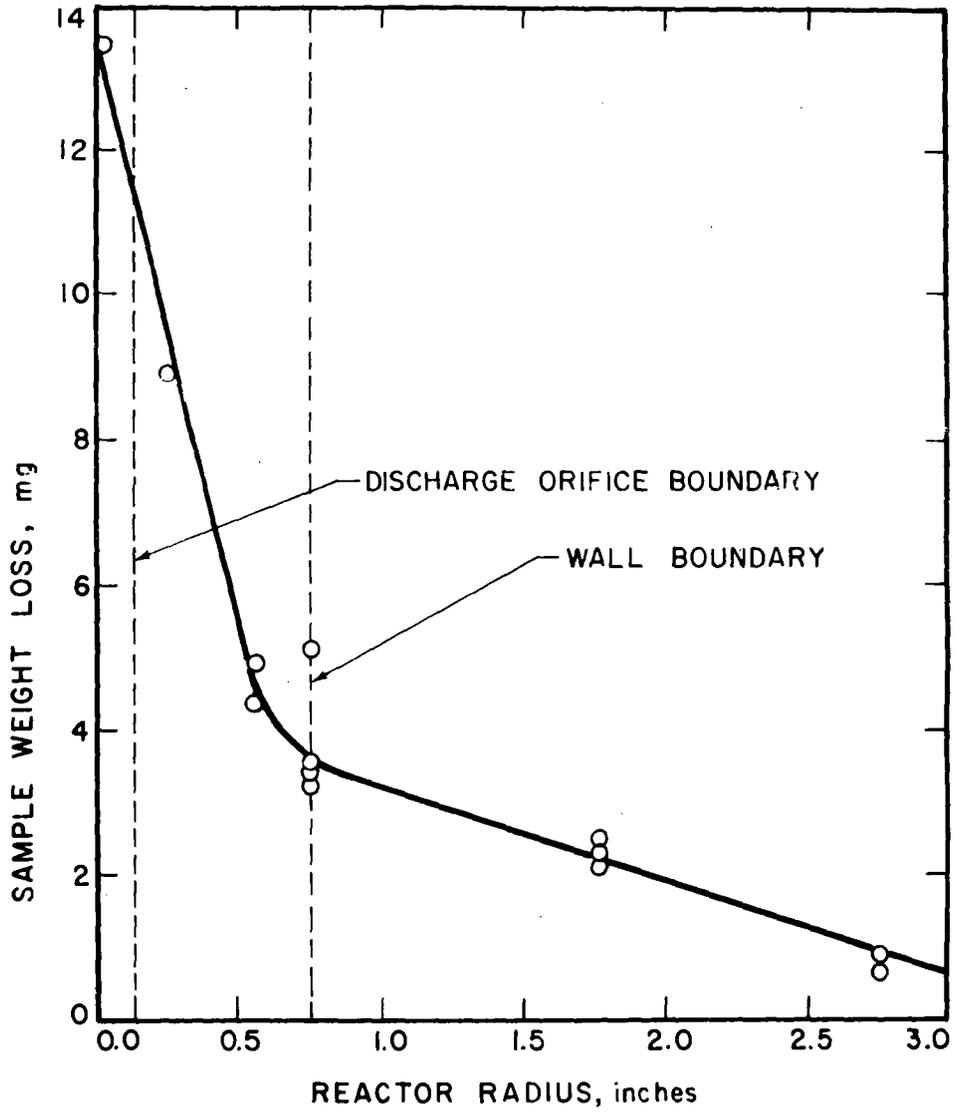


FIG. 4 THE INFLUENCE OF RADIAL DISTANCE ON THE WEIGHT LOSS OF POLYPROPYLENE