

# THE MANUFACTURE OF LEAD ACID BATTERY SEPARATORS USING LOCALLY PRODUCED POLYETHYLENE

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## ABSTRACT

*This study is an attempt to use the locally produced polyethylene in the manufacturing of lead acid battery separators as an economical substitute to the polyvinylchloride separator which is used in the lead acid batteries and produced by the state battery manufacturing company and also to the imported polyethylene separators.*

*This has been achieved by preparing mixtures of different percentages of the feed materials which include HDPE TR-160 locally produced, filler materials such as silica and oils such as DOP, paraffin which were added to the mixture to improve the final properties of the separator, the materials were compounded by two roll-mills under the same conditions. The best results of the feed materials in the mixture were selected so as to give the highest porosity and lowest electrical resistance using 15 wt.% PE, 30 wt.% filler, and 55 wt.% oil. It has been found that the films with DOP oil give higher porosity and lower electrical resistance than that made with paraffin oil but shows higher acid weight loss.*

## INTRODUCTION

Battery separator is an active component in the battery and play an important role to the cycle life and performance of the battery, thus, it made of thin sheet electrically insulating porous materials used as spacers between the plates (positive electrode and negative electrode) to prevent short circuit buckling of them while freely permitting to the ions to flow through the separator, absorb external mechanical forces to reduce the positive action mass, they also act as barriers to the transport of active materials between the plates and prevent dendrite formation<sup>(1,2)</sup>.

Broadly there are two categories of lead - acid battery separators skeletal and fiber structure separators, as their name imply skeletal separators are made of materials have a rigid inner structure such as polymers that has been fused by heat or chemical action and is mixed with filler typically precipitated silica, these separators are usually available with ribs which enable the separator to create an inter plate spacing while keeping overall separator mass to a minimum, an example of this kind of separators is the well known polyethylene type of material, the second class encompasses all those separators that have fibers as their basic material these fibers can be organic or inorganic and they can be found together with a resin or be laid together loosely without a binder, Both types of separators can be

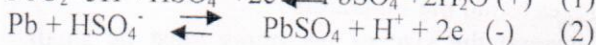
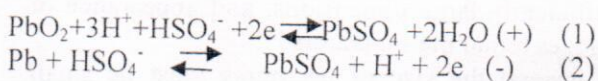
made available in sheet or in rolls depending on flexible and mechanically strong components of the battery<sup>(3)</sup>.

The present work can be divided to the following items:

1. Studying the effect of polyethylene addition as a binder on separator properties.
2. Studying the effect of filler addition as oil adsorbed on separator properties.
3. Studying the effect of the usage of two types of plasticizers on the final properties of separator.
4. Studying the effect of film thickness on the film properties.
5. Determining the suitable percentages of polyethylene, silica and plasticizer in the product film.

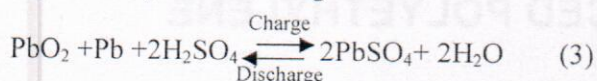
## Theory

According to the double sulfate theory<sup>(4)</sup> which proposed by Gladstone and Traube in 1882 the basic current generation process taking place in the lead acid batteries on the positive and negative electrode during charge and discharge may be written as the following reactions:



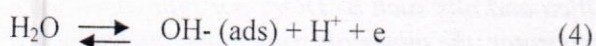


The net process while doing process is expressed by the following reaction:

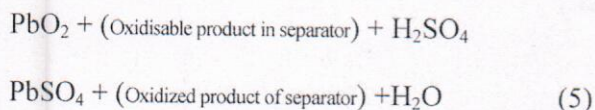


In this theory during the discharge of battery on both electrodes lead sulfate is formed due to the reduction of  $\text{PbO}_2$  on the positive electrode and the oxidation of spongy lead on the negative electrode.

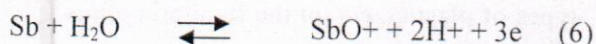
Kiseleva and Kabanov had studied the mechanism of the anodic evolution of oxygen on lead dioxide in sulfuric acid in detail and the rate of oxygen evolution is limited by the discharge step as:



The self-discharge of the positive plate may be related to the oxidation of separator materials



However in modern batteries the separator used made from materials which are practically not oxidized under the conditions of the positive electrode working and its reaction. During the anodic polarization of lead alloys in addition to the oxidation of lead other components of alloys such as antimony also undergo oxidation; the oxidation of antimony apparently proceeds according to the reaction:



Also an extreme sulfation of the negative plate is observed when the grid of the positive plate in battery contains an abnormally large percentage of antimony which then getting into the negative electrode across the pores of separator and lower the hydrogen overvoltage<sup>(4)</sup>. Another cause of short circuits at the edges of the plates and through the separator, is basically connected with an accumulation of sludge at the bottom of battery case owing to dissolution of the positive active mass then sludge particles are transferred electrophoretically to the negative plates lead to swelling of the active mass which penetrates the pores of the separators if it has sufficiently large dimensions, and appearance of bridges round the separators<sup>(5)</sup>. In general the size of the pores must be small enough to prevent the passage of solid materials

such as lead or lead sulfate crystals and to hinder the passage of antimony ions which frequently are introduced into the electrolyte by the positive plate and which migrate to the negative plate and there by shorten the life of the battery, but sufficiently large to permit the electrolyte to pass through<sup>(6)</sup>.

## EXPERIMENTAL WORK

### Compounding and Processing

These processes were done using of compounding laboratory equipment which is known as two-roll mills (figure(1)) where the pellets of polyethylene were compounded with high pressure exerted by two rolls compression about 800 psi, oil added gradually to the filler with continuous mixing then added to polyethylene and blended by repeat sheeting the mixture for (45) minute for homogeneity enhancing. This machine is made of two rolls of iron metals rotates one against each other at speed of operation 30 rpm and the length of each one (300 mm) and the diameter (228.6 mm), the feed charge in each stage of compounding was (150 to 200) g based on the total ingredients. After the period of compounding, materials mixture were introduced into a roll mill where rolls are heated by hot water of highly elevated temperature about 150 °C to be able to melt the polyethylene in the mixture for (10-15) minute to obtain finished sheet with thickness (0.2-0.35) mm.

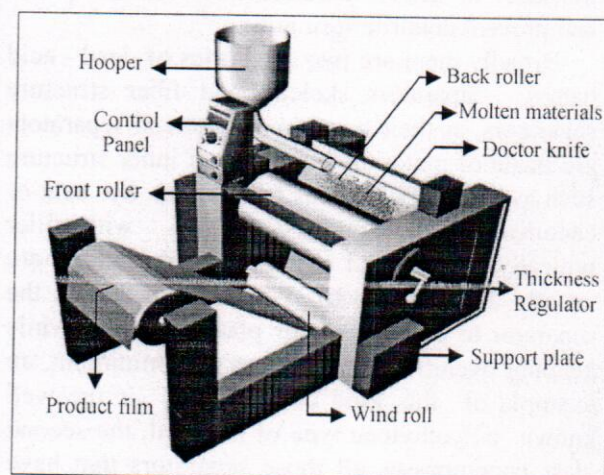


Figure (1): Schematic diagram of Compounding & Processing machine.



### Solvent Extraction Process

On a laboratory scale and for removing of processing oil from the films to produce separator has a suitable degree of porosity, the extraction process was done by using of 250 ml round bottom flask, a thermometer of 250 °C in one neck and a reflecting cooling water glass condenser (24 mm diameter and 470 mm height) fitted to the other for solvent vapor condensation, hot plate with magnetic stirrer to increase the washing efficiency of the films where solvent rotate continuously, water bath container used to control and regulate the temperature of the solvent. The oil extracted from films can be calculated as:

$$\text{The Oil extracted (\%)} = (W_0 - W_1)/W_0 \times 100 \quad (7)$$

### Solvent Recovery System

A non fractionated distillation (7) was used in laboratory distillation process, the distillation apparatus was employed consist of heating mental of 1.2 KW was connected to the voltage regulator to provide the input power, the heating mental was capable of 250 ml round bottom flask, a thermometer of 250 °C, and a glass condenser (35 mm diameter and 500 mm long) is connected with round bottom flask by help of glass connector as a divider using water as a cooling media.

### Tests and Measurements

#### Specific pore volume and Porosity

A Film of cross section area 40×40 mm<sup>2</sup> and thickness 0.25 mm were extracted, placed in an oven of 70 °C for about 60 minute to remove the moisture from them. The samples then were put in an evacuated dissecator for 24 hours to reach the room temperature, the film were weighed ( $W_1$ ) using electrical balance (4-digits) then immersed in a distilled water to become saturated at room temperature for 60 min and weight ( $W_2$ ) after that, therefore, the pore volume of the film can be represented as:

$$VP = (W_2 - W_1)/\rho_w \quad (8)$$

The total external volume of the film (VF) was measured by using mercury porosimeter

(available in the department of petroleum engineering).

Porosity (P) of the film was found by applying the equation (8,9):

$$P (\%) = V_p / V_F \times 100 \quad (9)$$

#### Electrical Resistance

The electrical resistance of the porous films in the cell was tested using of milliohmeter device (model 3130 hp) available in the State Battery Manufacturing Company, Babel -2 factory. The reading was recorded until stability is reached, specific gravity of sulfuric acid is 1.250 g/cm<sup>3</sup>.

#### Acid Weight Loss

The extracted films were dried and weighed ( $W_1$ ) then immersed in sulfuric acid with specific gravity 1.200 g/cm<sup>3</sup> which contained on 3%wt. of Potassium Dichromate in an oven at 60 °C for about 180 minute, then, the films were washed with distilled water and dried in an oven at 70°C to remove the moisture then put in an evacuated dissecator for 24 h to reach the room temperature. The films were weighed ( $W_2$ ). So the acid weight loss was determined by<sup>(6)</sup>.

$$\text{Acid weight loss (\%)} = (W_1 - W_2) / (W_1) \times 100 \quad (10)$$

#### Water Absorption

Large rectangular films were extracted, cut into (25.4×76.2) mm<sup>2</sup> and weighed ( $W_1$ ) then submerged in a boiled distilled water for about 120 minute then the saturated films were removed and cleaned with a peace of cloth piece to remove the water from the surface and then weighed it immediately ( $W_2$ ).

The weight gain of the films was found by applying the equation (10):

$$\text{Weight gain (\%)} = (W_2 - W_1) / (W_1) \times 100 \quad (11)$$

## RESULTS AND DISCUSSION

#### The Effect of Film Thickness

The effect of the film thickness on the oil extraction, porosity, and electrical resistance can be observed in figures (2) to (4), it has been found from figure (2) that when the film thickness increases (0.2, 0.25, 0.3, 0.35) mm, the extracted



oil decreases (49.67, 48.88, 47.75, 46.85) %, which means an increase of the remaining oil in the extracted film.

The porosity is also affected by the thickness changing; it has been found that the volume porosity decreases (42.76, 41.97, 40.49, 39.58) % with the increase in the film thickness as shown in figure (3). Figure (4) show the electrical resistance increase (34.9, 45.5, 59.2, 72.7) milliohm. inch<sup>2</sup> with the increase in the film thickness. The above results could be attributed to decrease in the solvent diffusion rate (increasing in diffusion resistance) with the increase in the film thickness due to the increase in the length of the micro channels presents between the filler particles and the binder which is occupied by the plasticizer.

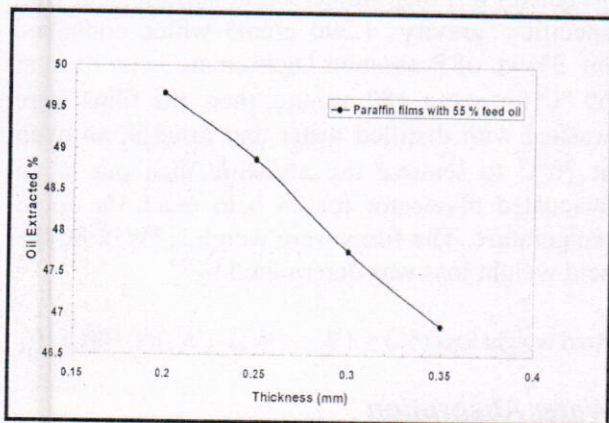


Figure (2) The effect of the film thicknesses on the film oil extracted at 60 minute extraction time and 25 °C extraction temperature.

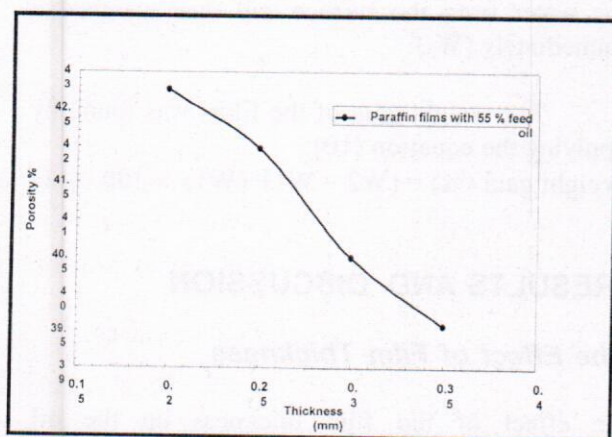


Figure (3) The effect of film thickness on the volume porosity.

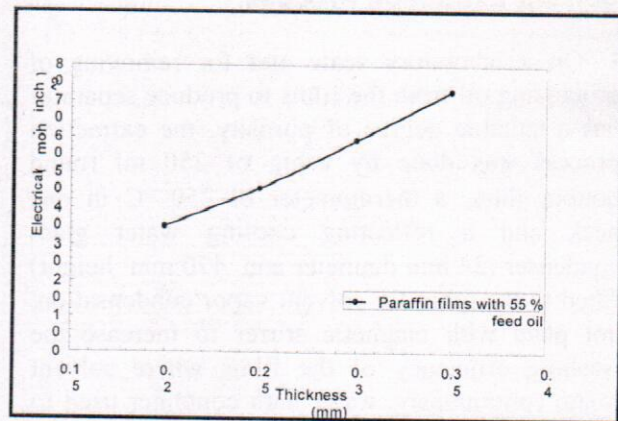


Figure (4) The effect of film thickness on the electrical resistance.

### The effect of Acid Oxidation

It has been found from figure (5) that the acid oxidation increases with the decrease of polyethylene content in the porous matrix which is considered the binder to other components of the film, this decrease in the polymer content with porosity increasing led to higher acid oxidation for the film due to the presence of inter channels which encourages the acid to diffuse and penetrate through the pores of the film easier and hence an increase of the polymer surface area that become in contact with the acid. From comparison between these two types of films it is explained that DOP films has a lower oxidation resistance than paraffin films due to increasing of its porosity. When the polymer content decreases the filler would have higher interaction between the polymer chains weakening the inner binding forces (weak bridges and covalent bonds of polymer) consequently the acid attack to the film increases, Schultz (11) proved that the weight loss represents an attack of strong acids on the carbon atoms removing them from the chains; therefore, as a result to this oxidation the polymer deteriorates leading to weight loss.

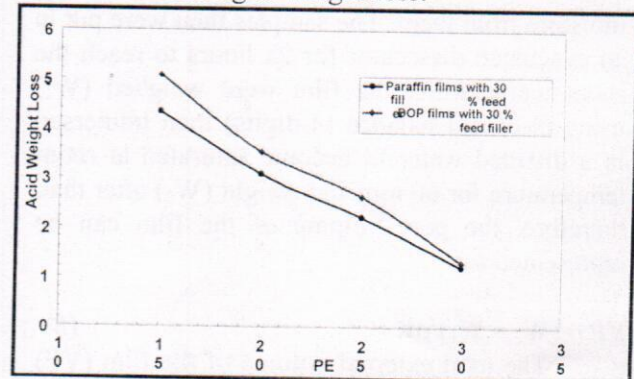


Figure (4) The effect of film thickness on the electrical resistance.



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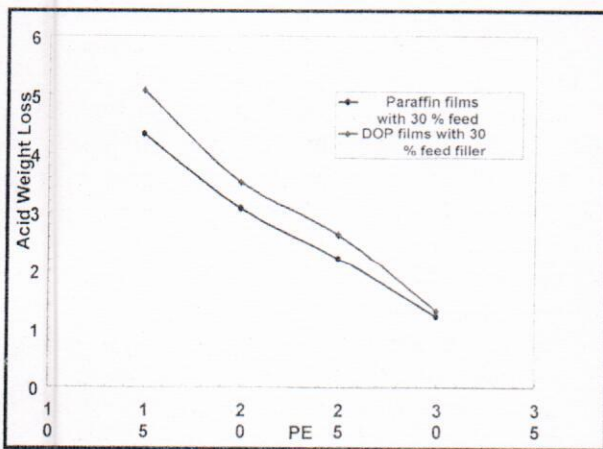


Figure (5) The effect of the polymer content on the films oxidation resistance with constant filler percent.

### The Effect of Porosity on Film Water Absorption

It has been observed from figure (6) that with increase the porosity the film weight gain increases rather linearly, hence the increase in porosity results from the presence of higher number of channels and patterns which increases the water itarance to the film.

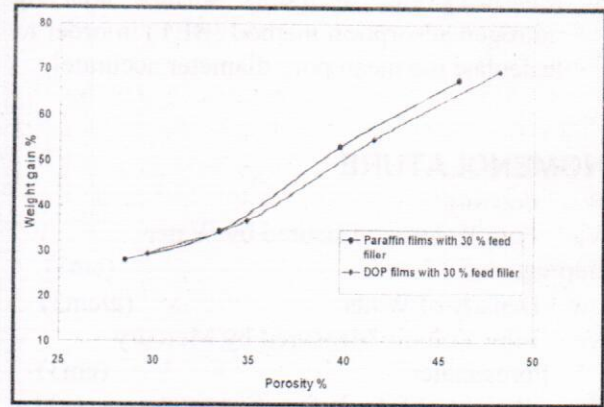


Figure (6) The effect of porosity on films weight gain with constant filler percent.

### CONCLUSIONS

From the present study, the following conclusions can be drawn:

1. The increase in film thickness led to decrease in oil extracted and hence reduction in the porosity and increase in electrical resistance.
2. Using DOP oil in film mixture gives rather better results of porosity and electrical resistance than that of paraffin oil.
3. Reduction in the polymer percent from (30 to 15) wt.% with increasing or fixation of filler feed percent will lead to porosity increase, reduction in electrical resistance, and increasing in film weight loss by acid.
4. The films acid weight loss increases with increasing the porosity.
5. Reducing of polymer feed percent with increasing of feed filler results in the appearance of some cracks and deformations during the processing by the two roll-mills.
6. The best percentages of film mixture was 15 wt.% PE, 30wt.% filler, and 55 wt.% oil to give the best porosity and electrical resistance.

### Recommendations for Further Work

- 1- Using other types of fillers such as kaolin, talc, or mica and comparison the results with that of silica fillers.
- 2- Using other types of oils that can dissolve in water like glycerol and comparing the results with that of DOP and paraffin oils.
- 3- Addition an antioxidant to the mixture to increase the film resistance to oxidation in the acid.



- 4- Measuring the separators surface area by nitrogen adsorption method (BET) in order to calculate the mean pore diameter accurately.

### NOMENCLATURE

P	Porosity	
$V_p$	Pore Volume Measured by Water	
Impregnated		(cm <sup>3</sup> )
$\rho_w$	Density of Water	(g/cm <sup>3</sup> )
$V_F$	Film Volume Measured by Mercury Porosimeter	(cm <sup>3</sup> )
$W_0$	Weight of Film before Extraction.	(g)
$W_1$	Weight of Dry Film after Extraction.	(g)
$W_2$	Weight of film impregnated with water.	(g)

### Abbreviations

BET	Brunauer, Emmet and Teller
DOP	Diocetylphthalate
HDPE	High Density Polyethylene
RPM	Revolution per Minute

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