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The Effect of Oil and Filer Contents on the Porosity of Lead Acid Battery Separators Produced From Polyethylene

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Abstract:

In this investigation a high density polyethylene (HDPE) was used as a substitute to polyvinylchloride in the production of lead acid battery separators. This has been achieved by preparing mixtures of different percentages of the feed materials which include a high density polyethylene (HDPE) locally produced, filler materials such as silica and oils such as dioctylphthalate (DOP) or 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 following parameters are involved:

1- Studying the use of a high density polyethylene as a binder to film components with (15-30) wt.%.
2- Studying the use of finely divided silica sand with (25-45) wt.% as a medium to oil adsorption.
3- Studying the use of two type plasticizers (Paraffin or DOP) with (35-55) wt. %. as a creative medium to films porosity.

The best results of the feed materials in the mixture were selected so as to give the highest porosity using 15 wt. % PE, 30 wt. % filler, and 55 wt. % oil. It has been found that the films with DOP oil give higher porosity.

Keyword: Lead Acid Battery Separator, Polyethylene, Film, Porosity.

Introduction:

Battery separator is the active component in the battery and plays an important roll to the cycle life and performance of the battery. It is made of thin sheet electrically insulating porous materials used as spacers between the plates (positive & negative) to prevent short circuit buckling of them while freely permitting to the ions in current to flow through the separator, absorb 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 (1,2).

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 (3).

The present work can be divided to the following items:

1. Studying the effect of the addition a high density polyethylene as a binder on separator properties.
2. Studying the effect of the addition a filler as oil adsorbed on separator properties.
3. Studying the effect of the usage of two types of plasticizers on the final properties of separator.

Theory:

According to the double sulfate theory(4) 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:

$$\mathbf{PbO_2 + 3H^+ + HSO_4^- + 2e \rightleftarrows PbSO_4 + 2H_2O \quad (+) \quad \ldots(1)}$$

$$\mathbf{Pb + HSO_4^- \rightleftarrows PbSO_4 + H^+ + 2e \quad (-) \quad \ldots(2)}$$

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

$$\mathbf{PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O \quad \ldots(3)}$$

In this theory during the discharge of battery on both electrodes lead sulfate is formed due to the reduction of **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:

$$\mathbf{H_2O \rightleftarrows OH^-_{(ads)} + H^+ + e \quad \ldots(4)}$$

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

$$\mathbf{PbO2 + (Oxidisable\ product\ in\ separator) + H_2SO \rightleftarrows PbSO_4 + (Oxidized\ product\ of\ separator) + H_2O} \quad \ldots(5)$$

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:

$$\mathbf{Sb + H_2O \rightleftarrows SbO^+ + 2H^+ + 3e} \quad \ldots(6)$$

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 over voltage(4).

Another one of the causes 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 (5).

In general that 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 (6).

Experimental Work:

1-Materials Used:

Polymer

High density polyethylene was used as a binder to the components of filler and plasticizer for producing films which is originally used for film applications, it was supplied by the State Company for Petrochemical Industries in Basrah in the form of pellets varies in particle size.

Silica Sand (Filler)

Local quartz silica sand is supplied by the State Company for Geological Survey and Mining, this type of filler was extracted from Urthumma quarry in Rutba area. In the present investigation it was used as adsorbent for plasticizer employed, for size reduction jet milling technique was used for this type of filler and the dust size which represented the finest particle size of the process were collected on the back filter of the system.

Plasticizers

In the present work two kinds of plasticizers were used paraffin oil and Dioctylphthalate for reaching to the best result of porosity and electrical resistance. With worth mentioning these oils were shared with some of experiments and extracted at the same conditions using n-hexane as a solvent.

2-Compounding and Processing

These processes were done with using of compounding laboratory equipment which known as two- roll mills (**Figure(1)**). 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 (12) inch and the diameter (9) inch, the feed charge in each stage of compounding was (150 to 200)g based on the total ingredients. The pellets of polyethylene were compounded with high pressure exerted by two rolls compression about 800 psi. Oil is added gradually to the filler (silica) with continuous mixing then blended with the polyethylene. The mixture were introduced into a roll mill where rolls are heated by hot water of highly elevated temperature about 150 ^{o}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. The arrangements of compositions for the experiments are tabulated in **Tables (1) and (2)**.

Solvent Extraction Process

On a laboratory scale and for removing of processing oil from the films (to produce separator with a suitable degree of porosity), the extraction process was done with using of 250 ml round bottom flask, a thermometer of 250 ^{O}C in one neck (**Figure(2)**) 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 for increasing of washing efficiency to the films where solvent rotate continuously, water bath container used to control and regulate the temperature of the solvent. The oil extracted can be calculated as:

The Oil extracted (%) = $\mathbf{(Woil_0 - Woil_1)/Woil_0 \times 100}$ .. **(7)**

Solvent Recovery System

A non fractionated distillation(7) was used in laboratory distillation process, the distillation apparatus (**Figure(3)**) 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 ^{O}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.

Volume Porosity

Films with 40×40 mm^2 cross section areas and 0.25 mm thickness 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 hr to reach the room temperature, the film were weighed **(W_1)** in an electrical balance (4-digits) then immersed in a distilled water for saturation at room temperature for 60 min and weighed **(W_2)** after that, therefore, the pore volume (**V_P**) of the film can be represented as:

$$V_P = (W_2 - W_1)/r_w \quad ..(8)$$

The total external volume of the film (V_F) was measured using mercury porosimeter (Ruska Instrument Corporation) available in the department of petroleum engineering.

Porosities of the films were found by applying the equation [8,9]:

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

The experimental results of oil extracted and porosity are tabulated in **Table (3)**.

Results and Discussion:

The Effect of Temperature on The Oil Extraction:

The effect of the temperature at which the oil extraction took place on the extracted and remaining oil are shown in **Fig.4**, It has been observed that with the increase of temperature from 25 to 65 ^{0}C, the increase of oil extracted were not significant. This is because of a high solubility of the plasticizer in n-hexane. At 65 ^{0}C the percentage of extraction did not exceed 1% compared at 25 ^{0}C. Therefore it is more economical to carry out the extraction at 25 ^{0}C.

The Effect of Time on the Oil Extraction:

The effect of extraction time on the oil extracted is shown in **Fig.5**. It is shown that as the sequence of extraction time (30,60,90,120) minutes, the extracted oil is (45.26,45.36,45.36,45.40)% respectively. Therefore a slight increase in the extracted oil with time could not be considered as a significant factor in time selection for best results (i.e., most of the oil feed in the original film mixture were dissolved in the early time of extraction). Again this is because of a high solubility of the plasticizer in n-hexane. According to theses results the increase of extraction time above 60 minutes is not necessary and this is considered the recommended time for this study.

The Effect of Separator Components on Porosity:

The capacity of lead acid battery can be improved by increasing of the porosity, to some level, beyond which the life time of battery may be reduced.

From **Figs.6 to 8** it has been shown that by increasing of the oil content the oil extracted increases too. The increase of oil content leads to an increase of the oil in the voids between the filler particles and on their surfaces which is extracted latter. Which can be explained that any increase in the oil content can be depleted in the extraction step. As seen in **Figs.6 and 7** the percentage oil extracted with DOP films is slightly higher than paraffin films. This is because DOP solubility in n-hexane is higher.

The changing of filler content of the film on the extracted oil is shown in **Fig.9**. It is clear from this figure that the increase in the filler content cause an increase in the oil extracted from the film. This because the aim of adding the filler is to form a surface where the oil can be spread on. Thus the increase in filler content leads to increase in the oil content and then increase in the oil extracted.

Figures.10, 11, and 12 show that as of the oil feed content increases the porosity of the film will increases. The extraction of the oil from the mixture led to the formation of pores and creating inner irregular tortuous channels which is responsible for the increase in the porosity. Although the increase in the oil content percentage on the expense of the polyethylene leading to an increase in the porosity, it is worth mentioning that the less polyethylene content the less the number of chains binding where the filler grains will increases the wettability and may lead to more open pores and channels making the penetration and diffusion of the solvent through the film more easier. This behavior were also confirm through fixation of oil feed percentage, decreasing in the feed polymer percent, and increasing in the filler percentage where the oil is adsorbed and distributed over higher amount of filler particles leading to an increase in the number of the inner channels occupied by oil which is going to be opened by extraction process, the results were an increase in the porosity.

By comparison between the films made of paraffin oil and that made with DOP oil it had been found that the porosity of the first is less than that of the latter. This is explained previously, the higher solubility of DOP than paraffin oil in organic solvents (i.e.,. oil extracted from DOP samples is rather higher than paraffin oil samples).

An increase in porosity is gained as the filler content increases (**Fig.13**). Again this behavior was explained earlier, that is the increases in filler content leads to increase in the oil content, thus increase the porosity of the film.

Conclusions:

1- The best conditions for oil extraction were 60 minutes at 25 ^{0}C.

2- The decrease in oil extracted cause a reduction in the porosity.

3- The increase of the oil feed percent in the film mixture from (35 to 55) wt. % led to a noticeable increase in porosity after its extraction through creation of pores.

4- Using DOP oil in film mixture gives rather better results of porosity.

5- The increase in (polymer/filler) ratio results in the reduction in films porosity.

6- Reduction in the polymer percent from (30 to 15) wt.% with increasing or fixation of filler feed percent will lead to porosity increase.

7- The best percentages of film mixture was 15 wt.% PE, 30wt.% filler, and 55 wt.% oil to give the best porosity.

Nomenclature:

P	Porosity
V_F	Film Volume Measured by Mercury Porosimeter (cm^3)
V_P	Pore Volume Measured by Water Impregnated (cm^3)
W_1	Weight of dry film after extraction. (g)
W_2	Weight of film impregnated with water. (g)
$Woil_0$	Weight of Film before Extraction. (g)
$Woil_1$	Weight of Dry Film after Extraction. (g)
ρ_w	Density of Water (g/cm^3)

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Table (1): The arrangement of paraffin films experiments.

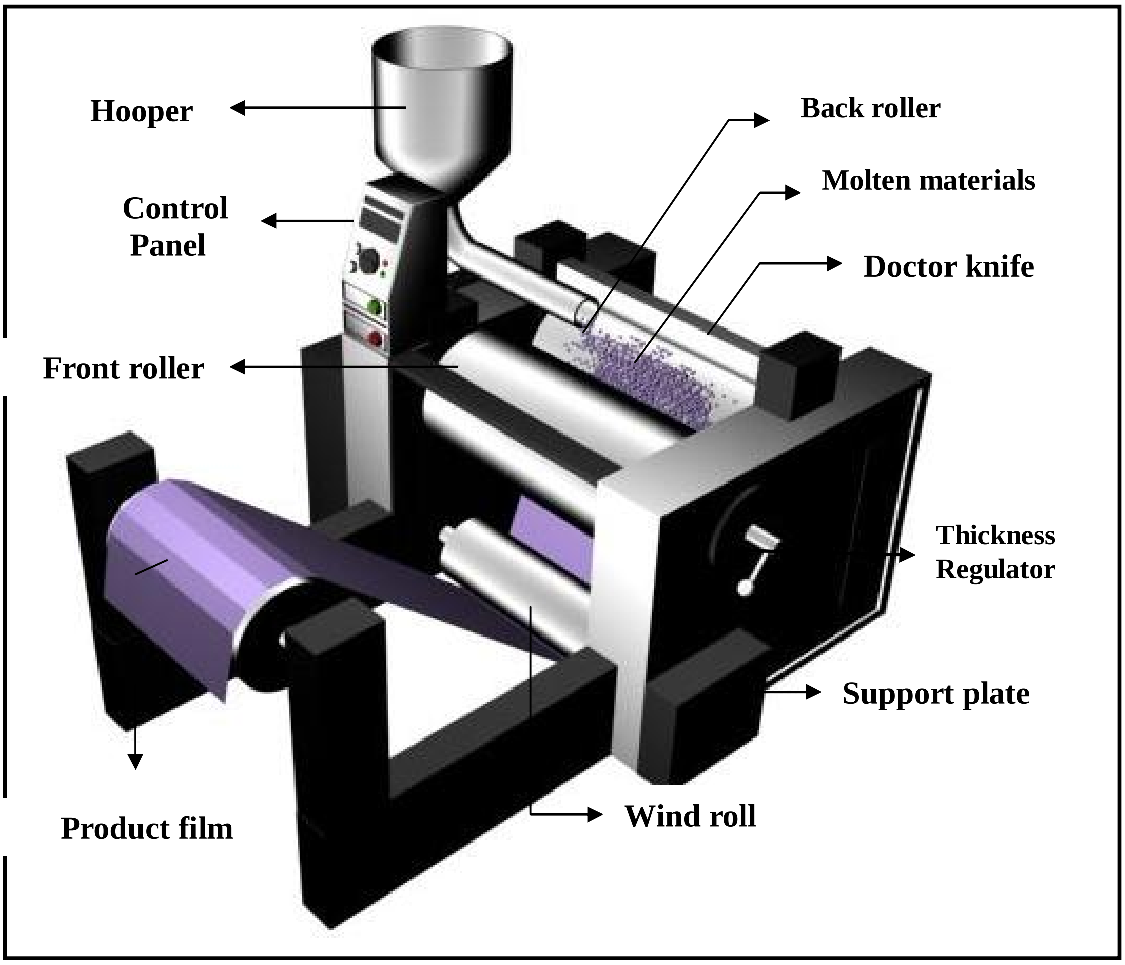
Set. No	Exp. No	Polyethylene Wt. %	Silica Wt.%	Paraffin Oil Wt.%
One	1	30	30	40
	2	25	30	45
	3	20	30	50
	4	15	30	55
Two	5	30	35	35
	6	25	35	40
	7	20	35	45
	8	15	35	50
Three	9	20	25	55
	3	20	30	50
	7	20	35	45
	10	20	40	40
Four	1	30	30	40
	6	25	35	40
	10	20	40	40
	11	15	45	40

Table (2) The arrangement of DOP films experiments.

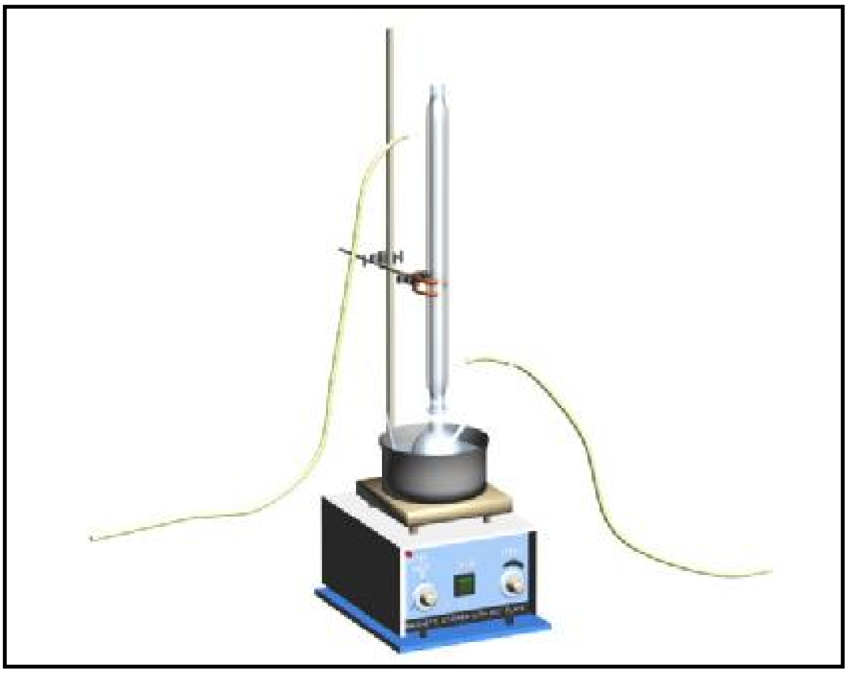
Set. No	Exp. No	Polyethylene Wt. %	Silica Wt.%	DOP Wt.%
One	1	30	30	40
	2	25	30	45
	3	20	30	50
	4	15	30	55
Two	9	20	25	55
	3	20	30	50
	7	20	35	45
	10	20	40	40
Three	1	30	30	40
	6	25	35	40
	10	20	40	40
	11	15	45	40

Table (3) Results of Oil extraction from DOP & Paraffin films.

Set. No	Exp. No	Oil Content Wt. %	Oil Extracted wt.%		Porosity %	
			Paraffin	DOP	Paraffin	DOP
One	1	40	34.69	35.58	28.51	29.71
	2	45	40.58	42.26	33.46	34.93
	3	50	45.30	47.07	39.74	41.53
	4	55	49.42	51.38	45.99	48.17
Two	5	35	32.47	……..	30.36	……..
	6	40	35.69	36.79	32.59	33.98
	7	45	40.45	41.99	38.14	39.70
	8	50	46.74	……..	43.22	…….
Three	9	55	48.88	50.73	41.97	43.91
	3	50	45.30	47.07	39.74	41.53
	7	45	40.45	41.99	38.14	39.70
	10	40	36.90	38.21	36.52	38.01
Four	1	40	34.69	35.58	28.51	29.71
	6	40	35.69	36.79	32.59	33.98
	10	40	36.90	38.21	36.52	38.01
	11	40	38.35	39.57	39.03	41.38



Fig(1) Schematic diagram of Compounding & Processing machine.



Fig(2) Schematic diagram of extraction process

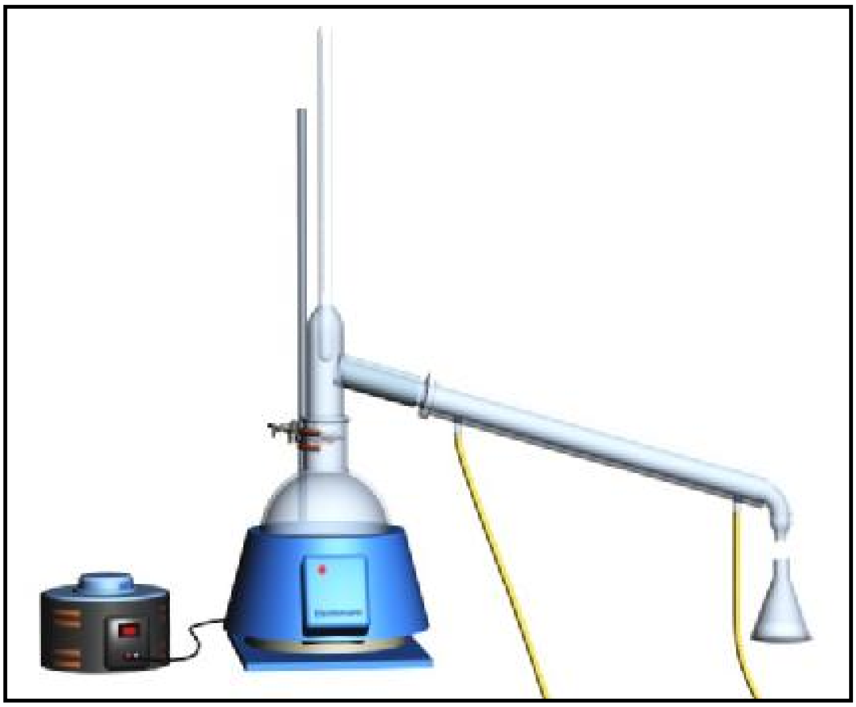


Figure (3): Schematic diagram of solvent recovery method

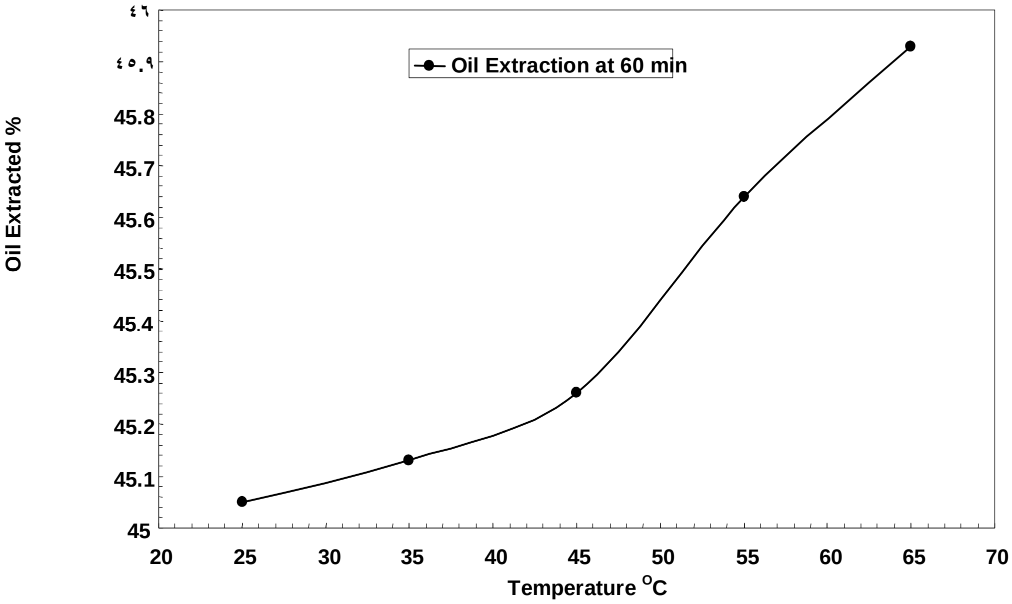


Figure (4): The effect of the solvent temperature on the film oil extracted.

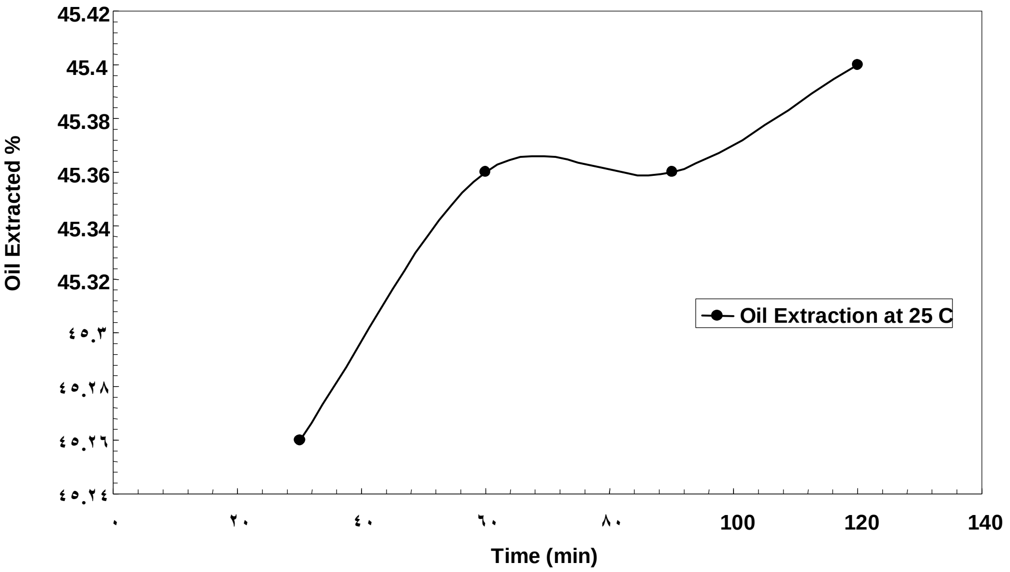


Figure (5): The effect of the extraction time on the film oil extracted.

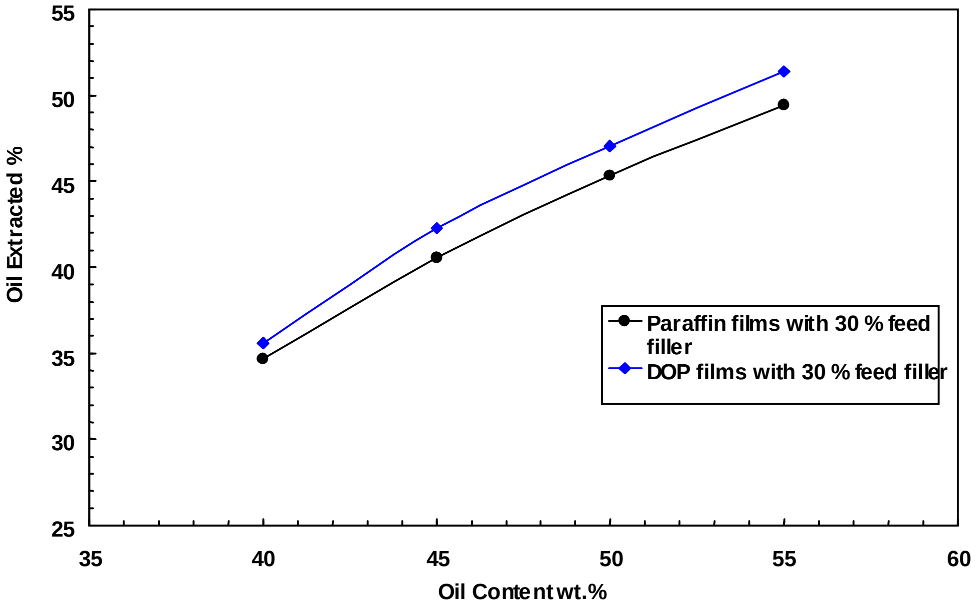


Figure (6): The effect of the oil feed percent on the film oil extracted with constant filler percent.

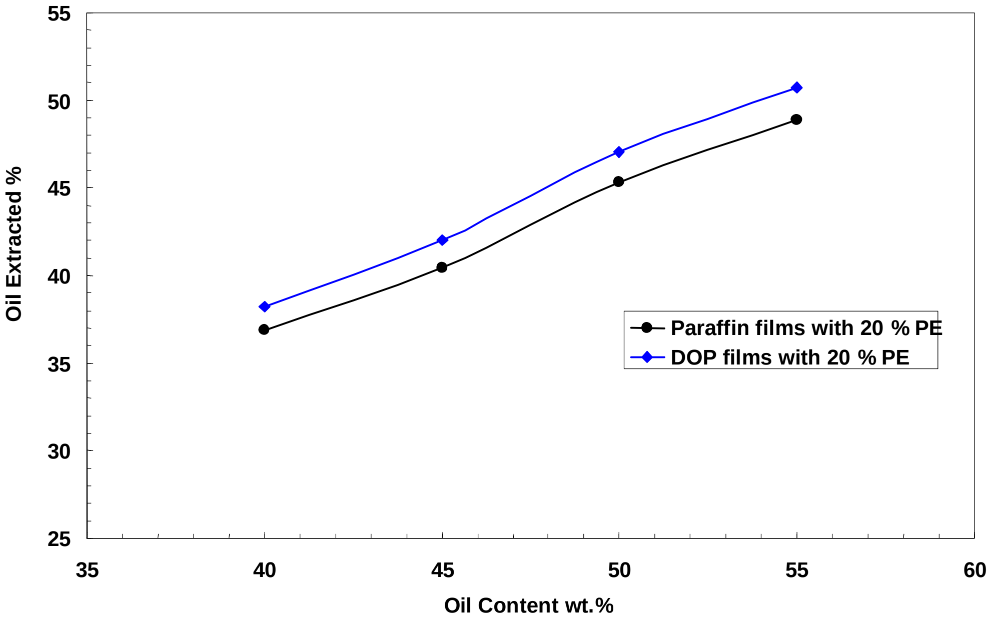


Figure (7): The effect of the oil feed percent on the film oil extracted with constant polymer feed percent.

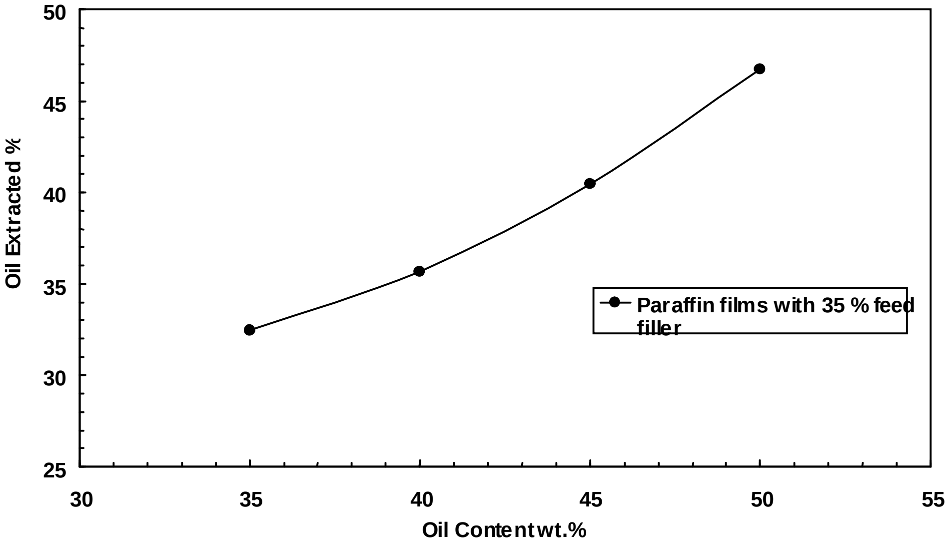


Figure (8): The effect of the oil feed percent on the film oil extracted with constant filler percent.

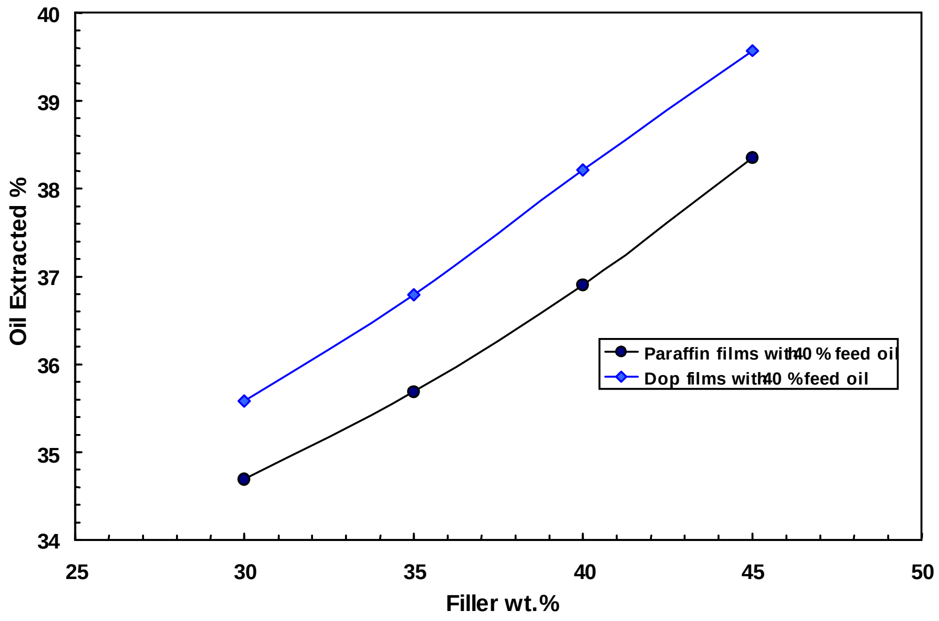


Figure (9): The effect of filler content on the extraction efficiency with constant oil feed percent.

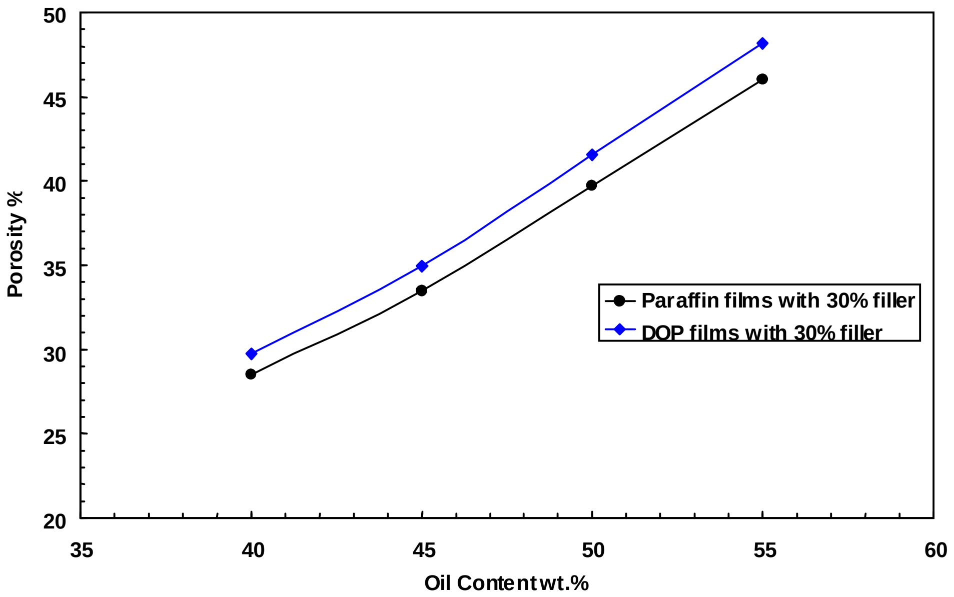


Figure (10): The effect of the oil feed percent on the film porosity with constant filler percent.

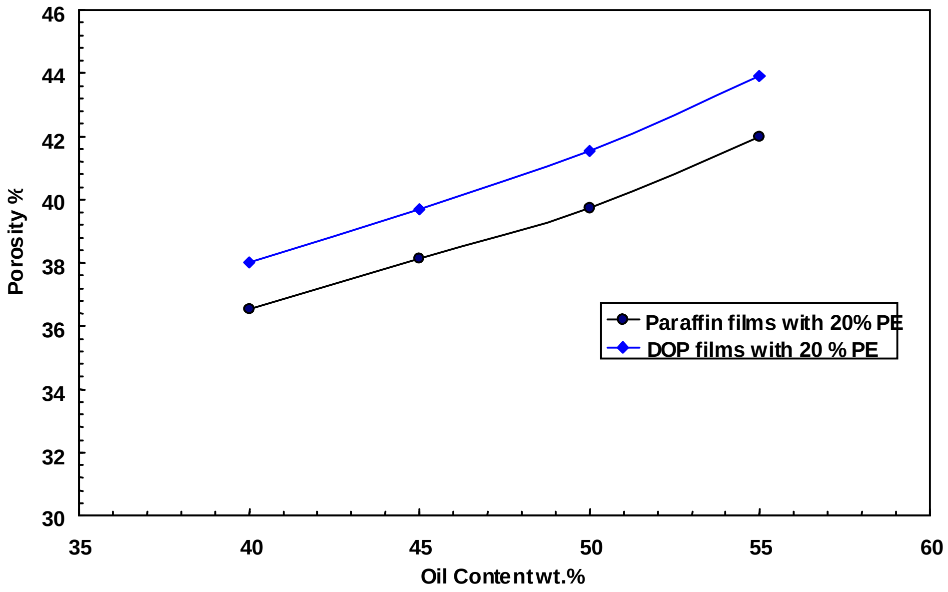


Figure (11): The effect of the oil feed percent on the film porosity with constant polymer feed percent.

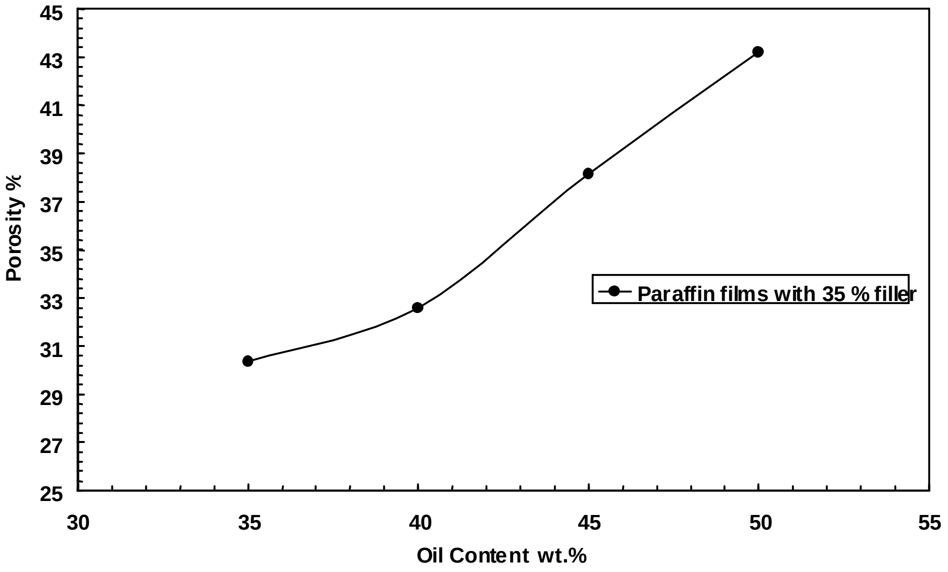


Figure (12): The effect of the oil feed percent on the film porosity with constant filler percent.

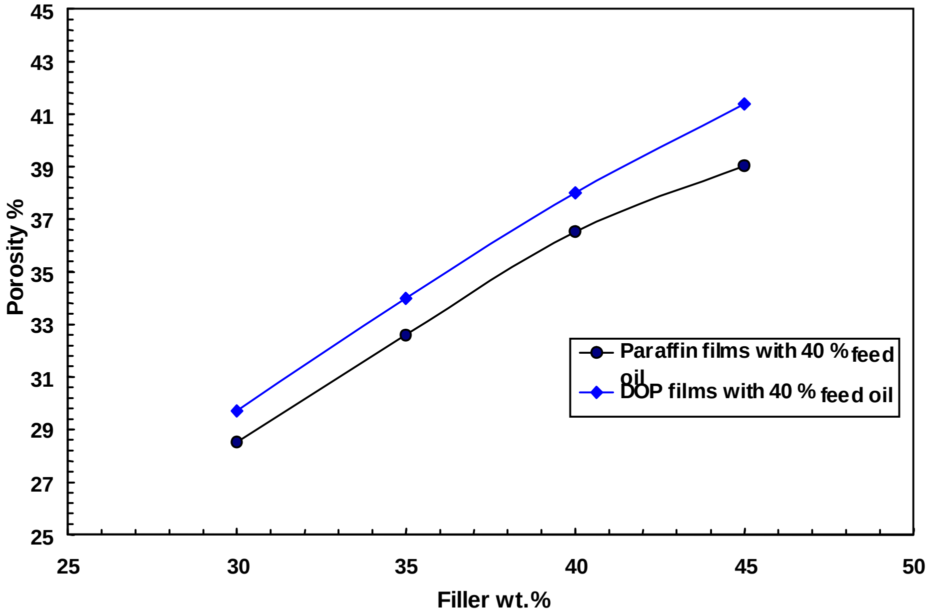


Figure (13): The effect filler content on the film porosity with constant oil feed percent.

تأثير المكونات من الزيت والمالأت في الفراغية لعوازل بطاريات الرصاص السائلة المصنوعة من البولي اثيلين

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الخلاصة :

يتناول هذا البحث دراسة استخدام البولي اثيلين المنتج محليا في تصنيع عوازل بطاريات الرصاص السائلة كبديل اقتصادي عن عوازل البولي فينيل كلورايد المستخدمة من قبل الشركة العامة لصناعة البطاريات وكذلك عن عوازل البولي اثيلين المستوردة .

تم ذلك من خلال تحضير خلطات بنسب مختلفة للمواد الداخلة والتي تشمل البولي اثيلين عالي الكثافة ، مواد مالئة مثل السليكا، زيوت مثل البارافين اوثنائي اوكتايل الفثاليت (الدوب) التي تضاف إلى الخلطة لتحسين الخواص النهائية للعازل ، ثم تشكيله بواسطة ماكنة الخلط والمعروفة **two – roll mill** بظروف عملية ثابتة .

تضمن البحث المحاور آلاتية

-استخدام البولي اثيلين العالي الكثافة بنسب وزنية ١٥-٣٠ %.
-إضافة مادة السيليكا بنسب وزنية ٢٥-٤٥%.
-تأثير إضافة مادة ملدنة (لعمل الفراغات) مثل زيت البرافين و الدوب بنسب وزنية ٣٥ -٥٥%.

تم تحديد أفضل النسب للمواد الداخلة في الخلطات والتي أعطت أعلى درجة من المسامية باستخدام البولي اثيلين العالي الكثافة بنسبة (١٥) %, مواد مالئة بنسبة (٣٠) % و(٥٥) % من الزيت ، لقد وجد بان النماذج مع زيت ثنائي اوكتايل الفثاليت تمتاز بدرجة مسامية أعلى عن نماذج زيت البرافين .