Grasas y Aceites
Vol. 52. Fasc. 5 (2001), 317-322

Thermal stability of some metal-palmitate soaps which find various industrial applications

By **M.F.R.Fouda***, **Elham A.A.Yousef****, **S.S.Mohamed**** and **late Zein E.Shoeb****

* Inorganic Chemistry Department, National Research Centre, Cairo, Egypt
** Fats and Oils Department, National Research Centre, Cairo, Egypt

RESUMEN

Estabilidad térmica de jabones metal-palmitato con diversas aplicaciones industriales

Se han preparado jabones de tierras alcalinas y elementos de transición y orbitales "d" completos por el método de la descomposición doble mediante la reacción entre sales metálicas y palmitato sódico. La estabilidad térmica de estos jabones se estudio con el fin de arrojar luz sobre su idoneidad para su uso como catalizadores o lubricantes. Se encontró que los jabones de las tierras alcalinas son más estables que los de transición y que los jabones con la capa "d" completa.

PALABRAS-CLAVE: Catalizador – Estabilidad térmica – Jabón metal-palmitato – Lubricante.

SUMMARY

Thermal stability of some metal-palmitate soaps which find various industrial applications.

The soaps of alkaline earth's and transition elements and closed 'd' orbitals were prepared by the double decomposition method by the reaction between metallic salts and sodium palmitate. The thermal stability of these soaps was studied in order to throw the light on their suitability for using as catalysts or lubricants. The soaps of alkaline earth's were found to be more stable than transition and 'd' closed shell soaps.

KEY-WORDS: Catalyst – Lubricant – Metal-palmitate soap – Thermal stability.

1. INTRODUCTION

Metallic soaps are a group of water-insoluble compounds containing alkaline earth's or heavy metals combined with monobasic carboxylic acids of 7 to 22 carbon atoms. These soaps find wide applications in various fields. They are used as stabilizers for plastics (1-3), as fungicides (4), catalysts (5), driers (6-7) fuel additives (8) as additive for lubricants and some pharmaceutical formularies (9) and as oil spill absorbent materials [i.e for removing of petroleum from water (10)].

The acid or anion portion of a metal soap can be varied. Typical anions currently used are rosin and tall oil fatty acids, saturated and unsaturated naturally-occurring long-chain monocarboxylic fatty acids with 7 to 22 atoms, naphthenic, 2-ethylhexanoic, and the newer synthetic tertiary acids.

Acid soaps contain free acid (positive acid number), whereas neutral (normal) soaps contain no free acid (zero acid number). That is, the ratio of acid equivalents to metal equivalents is greater than one in the acid soap and equals to one in the neutral one. The basic soap is characterized by a higher metal-to-acid equivalent ratio than the normal metal soap where particular properties are obtained by adjusting the basicity.

The present study deals with a number of neutral metallic soaps prepared and characterized by several thermal and spectroscopic techniques such as infrared spectra and X-ray diffraction patterns.

The present study aimed to investigate their molecular structure and their stability towards heat.

2. EXPERMENTAL

Preparation of soaps

The studied soaps were prepared by gradual addition of the stechiometric amounts of a warm solution of 10% sodium palmitate dissolved in 10% ethanol water mixture, while stirring, to 5% aqueous solution of chloride or nitrate of Mg, Ca, Sr, Ba, Mn, Fe, Ni, Cu, Zn, and Ag until complete precipitation of the desired metallic soap. The proposed sequence for addition was followed to avoid the precipitation of the corresponding metal hydroxides.

The precipitated metallic soaps were washed thoroughly with water until the wash was free from chloride or nitrate ions .The resulted products were dried, at 40°C for several days until constant weight was achieved before use.

Techniques and measurements

The infrared absorption spectra, IR were measured using Lambda 40 and FTIR Spectrum 1000 respectively (11-13).

X-ray powder diffraction for the examined compounds patterns were obtained at room temperature using a Siemens diffractometer (D 500) employing Ni-filtered Cu Kα radiation (λ=1.5404A). The X-ray tube was operated at 36 KV and 20 mA samples were finely ground and packed in a plastic

Table I

The frequencies (cm^{-1}) of absorption maxima in the IR spectra of alkaline earth's palmitate form

Metallic Soap	- OH (H_2O)	Aliphatic stretched bands	>C=O	$-COO^-$ asym / $-COO^-$ sym	CH_3-	$-CH_2$	Progressive $-CH_2$	C-O
$Mg(Pal)_2$	3413 3320	2960 2915 2850	----	1560 1430	1380	1460	1190,1300, 1280,1260, 1240	1110
$Ca(Pal)_2$	3420 (br)	2960 2917 2846	1700	1583 1430	1380	1460	1400,1350, 1330,1320, 1280,1258 1230,1210 1190,1120	1100
$Sr(Pal)_2$	3432(br)	2960 2917 2848	1700	1513 1403	1370	1469	1334,1319, 1292,1232, 1209,1187	1099
$Ba(Pal)_2$	3420	2960 2915 2846	1700	1509 1403	1370	1469	1319,1297, 1276,1232, 1211 1187	1099

Table II

The frequencies (cm^{-1}) of absorption maxima in the IR spectra of transition element's palmitate form

Metallic Soap	- OH (H_2O)	Aliphatic stretched bands	>C=O	$-COO^-$ asym / $-COO^-$ sym	CH_3-	$-CH_2$	Progressive $-CH_2$	C-O
$Mn(Pal)_2$	3413 3320	2960 2917 2848	----	1560 1427	1380	1467	1317,1300 1275,1250 1230,1210	1110, 1118
$Fe(Pal)_3$	3737 (br)	2960 2919 2848		1571 1420	1380	1456	1317,1300 1275,1250 1230,1210 1190	1100
$Ni(Pal)_2$	3440(br)	2960 2917 2848	1700	1560 1440	1380	1467	1320,1300 1280,1250 1230,1210 1190	1112
$Cu(Pal)_2$	3440	2960 2913 2848		1583 1440	1380	1467	1320,1300 1280,1250 1230,1210 1190	1099
$Zn(Pal)_2$	3432(br)	2960 2915 2846		1538 1398	1375	1463	1320,1300 1280,1260 1238,1210 1190 .	1100
Ag -Pal	3448	2960 2915 2846		1558 1517 1419	1380	1471	1350,1335 1320,1300 1280,1250 1230,1210 1190	1100 1118

holder. The diffraction angle (2θ) was scanned at rate of 2θ min^{-1} (14).

The metal soaps are subjected to thermal analysis using Perkin-Elmer, 7 series thermal analysis system with a differential scanning calorimeter cell. The rate of heating was 10°C/min in a stream of air with a flow rate of 30 cm^3/min.

3. RESULTS AND DISCUSSION

Infrared spectra of palmitates

The different palmitates were characterized by means of recording of their infrared spectra (Tables I and II). They possess the following characteristics:

(a) Presence of characteristic progressive (CH_2) bands which lie between 1150 and 1390 cm^{-1} (12) and a deformation one which lies at (1456-1467) cm^{-1}.

(b) Presence of three stretch bands lie in 2960,2915 ± 4,and 2846 ± 4 cm^{-1} of the aliphatic chain .

(c) Presence of characteristic COO^-sym and COO^-asym bands at 1420 ± 20 & 1570 ± 10cm^{-1} respectively.

(d) Appearance of characteristic bands for methyl group at 1370 or 1380 cm^{-1} depending on the nature of the metal .

Thermal gravimetric analysis of some metal palmitates

The different palmitates suffer from stability on heating at relatively high temperature and transform to oxide or carbonate depending on the identity of the

Table III

Characterization of TG and DTG curves for alkaline earth's soaps

Metallic Soap	Thermal Step	Thermal Range	Loss%		Thermal Product
			Actual	Calculated	
$Mg(Pal)_2$	dehydration step	50-128	-----		
	decomposition	400-443	12.17	15.75	$MgCO_3$
	decomposition	>>443	6.96	7.53	MgO
$Ca(Pal)_2$	dehydration step	50-140	------		
	decomposition	445.5-487.7	16.5	16.5	$CaCO_3$
	decomposition	487.7-682.5	10	10.178	CaO
$Sr(Pal)_2$	dehydration step	64.8-185.7	-----		
	decomposition	492.8-512	24.6	24	$SrCO_3$
	thermal stability	512-800			
	decomposition	>>800	17.4	17.3	SrO
$Ba(Pal)_2$	dehydration step	50.8-181.8	-----		
	decomposition	>>856	30.8	30.44	$BaCO_3$

metal as clarified in Table III. The resulting compounds were characterized by means of x-ray diffraction patterns where they show the characteristic 'd' spacings according to ASTM (15) cards N° 4-829, 28-775, 6-520, 41-373,41-1442, 4-755, 5-664,4-835, 5-661,4-783 for MgO, CaO, SrO, $BaCO_3$, Mn_2O_3, Fe_2O_3, ZnO, NiO, CuO, and Ag respectively (Tables IV and V).

The soaps of barium palmitate and magnesium palmitate were taken as a representative example for investigation of the thermal behavior of alkaline earth soaps. The courses of TG (Thermal Gravimetry) and DTG (Derivative Thermal Gravimetry) plots of barium palmitate clarified that the soap starts to loss its water of hydration at 50.8°C ending at 180.8°C with formation of an anhydrous soap. The last compound suffers from stability at higher temperatures and transforms to the corresponding carbonate at 600°C. The last compound transforms to the oxide at temperatures higher than 856°C (Figure 1).

By analogy the thermal behavior of the palmitates of Mg,Ca and Sr were more or less the same as that of barium palmitate. In case of heating of Magnesium palmitate (Figure 2) the resulting of Magnesium carbonate at 400°C and MgO resulted at > 443 °C. MgO was confirmed by appearance of their characteristic d spacing published by ASTM (15), cards N° 4-829 (Figure 3).

Generally speaking the transformation of carbonates into the corresponding oxides in case of alkaline earth soaps depends on the heating temperature and the basicity of metal, since it is known that the carbonates of basic metals decomposed at higher temperatures i.e the

Table IV

Characteristics of d°A spacings of the heated metal palmitat product and of silver palmitate

MgO		CaO		SrO		$BaCO_3$		Mn_2O_3		Fe_2O_3		ZnO		NiO		CuO		Ag		Ag-Pal	
d°A	I/I° *	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°
2.43	13.5	3.04	100	3.0	56	4.5	8	3.95	35.3	2.96	47.6	2.82	89.8	2.41	66.3	2.75	12.9	2.36	100	21.5	100
2.11	100	2.5	19	2.59	48	3.7	81	2.77	100	2.52	100	2.61	64.8	2.09	100	2.52	100	2.05	30	14.6	92.9
1.49	43.2	2.28	24.6	1.82	100	3.66	40.5	2.39	29.4	2.09	19.1	2.48	100	1.47	50	2.32	94.3	1.44	32.9	10.9	47.6
1.27	10.8	2.09	20.1	1.55	32	3.22	100	2.03	23.5	1.76	14.3	1.91	31.8	1.25	20	1.87	27.1	1.23	30	8.71	42.9
1.21	13.5	1.91	21.7	1.48	32	3.03	16	1.92	11.8	1.61	28.6	1.63	48.9	1.21	15	1.71	9.9	1.18	8.6	7.3	16.7
		1.87	23.1	1.28	68	2.74	10.8	1.86	17.7	1.48	30.1	1.48	33			1.58	14.3			5.5	9.5
				1.19	36	2.65	5.4	1.68	35.3			1.41	6.8			1.51	18.6			4.63	9.5
						2.62	32.4					1.38	30.7			1.42	11.4			4.52	11.9
						2.6	18.9					1.36	14.8			1.38	17.1			3.48	4.8
						2.58	18.9					1.3	6.8			1.3	5.7			3.45	4.8
						2.3	5.4					1.23	6.8			1.27	8.6				
						2.1	27														
						2.08	18.9														
						2.01	24.3														
						1.94	54.1														
						1.93	35.1														
						1.86	8.1														
						1.7	8.1														
						1.65	8.1														
						1.63	8.1														
						1.61	16.2														
						1.56	10.8														
						1.51	13.5														
						1.37	16.2														
						1.36	10.8														
						1.33	10.8														

* I/I° Shows the ratio of the height of the given peak to the height of the most intense peak in the given pattern .

Table V
Characteristics of d°A spacings of some metal oxides, silver and of silver palmitate as astm cards

MgO		CaO		SrO		$BaCO_3$		Mn_2O_3		Fe_2O_3		ZnO		NiO		CuO		Ag		Ag-Pal	
d°A	I/I° *	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°	d°A	I/I°
2.431	9	3	100	2.98	69	4.49	9	3.84	11	2.95	29	2.816	62	2.41	79	2.75	11	2.359	100	21.4	100
2.106	100	2.52	24	2.581	88	3.691	100	2.71	100	2.52	100	2.602	53	2.088	100	2.53	47	2.044	46	14.5	92
1.489	74	2.28	79	1.825	100	3.646	49	2.35	16	2.09	29	2.476	100	1.476	81	2.32	100	1.445	41	10.9	31
1.27	7	2.09	57	1.556	73	3.22	71	2	11	1.7	18	1.911	38	1.259	27	1.866	32	1.23	50	8.75	42.9
1.216	21	1.91	94	1.49	38	3.03	6	1.92	1	1.61	52	1.626	61	1.206	23	1.71	11	1.179	24	7.32	23
		1.88	96	1.29	25	2.74	3	1.845	13	1.48	90	1.477	59			1.58	21			5.48	6
				1.184	39	2.67	3	1.66	46			1.407	11			1.505	32			4.59	65
						2.62	30					1.379	50			1.418	20			4.52	66
						2.61	20					1.359	26			1.375	33			3.48	96
						2.56	37					1.3	6			1.3	13			3.45	97
						2.33	3					1.238	10			1.265	11				
						2.123	59														
						2.089	28														
						2.03	27														
						2.008	53														
						1.94	44														
						1.84	8														
						1.82	4														
						1.709	4														
						1.68	2														
						1.652	22														
						1.55	12														
						1.54	5														
						1.37	11														
						1.36	22														
						1.35	22														

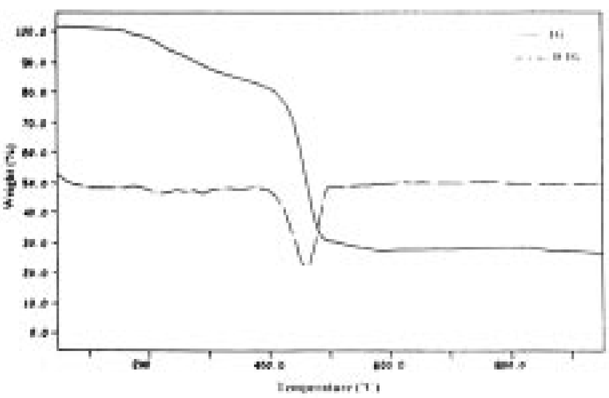

Figure 1
TG and DTG of Barium palmitate (heating rate = 10 °C/min)

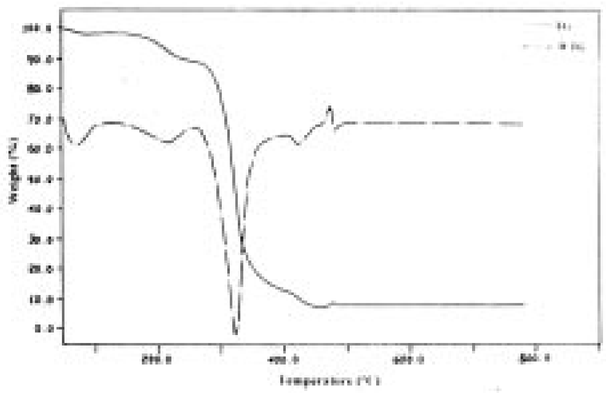

Figure 2
TG and DTG of Magnesium palmitate (heating rate = 10 °C/min)

decomposition temperatures of alkaline earth carbonate increase in the following sequence $MgCO_3$<$CaCO_3$< $SrCO_3$<$BaCo_3$ (16).

The identity of carbonates was also confirmed by the presence of their characteristic CO_3^{-2}, C=O and C-O bands (Table VI) and disappearance of that characteristic for methyl group, progressive - CH_2 groups and aliphatic chain.

As can be seen from Table III and Figures 1 and 2 the temperature of conversion of such compounds to the corresponding carbonates and oxides was found to increase with increasing the basicity of the alkaline earth's metals as could be expected.

The palmitates of transition elements and closed 'd' orbitals suffer from stability by heating and show different decomposition steps not isolated with a reasonable range of constancy.

The heating process of different transition elements leads to formation of the corresponding oxide Fe_2O_3, Mn_2O_3, NiO, CuO and ZnO as end

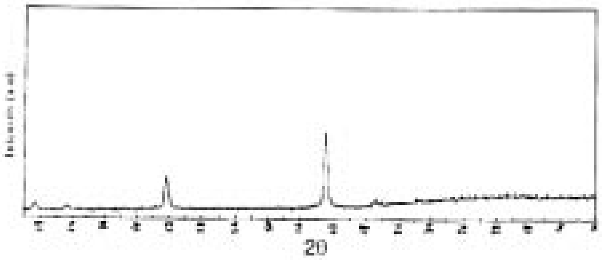

Figure 3
X-Ray diffraction pattern of Magnesium Oxide (MgO).

Table VI
The frequencies (cm^{-1}) of absorption maxima in the IR spectra of alkaline earth's carbonated form

Metallic Soap	Frequency cm^{-1}					
	CO_3^{-2}	C=O	C-O	Aliphatic bands	$-CH_2-$ progressive	$-CH_3$
$MgCo_3$	1400-1462	1700	—	—	—	—
$CaCo_3$	1428(br)	1797	—	—	—	—
$SrCo_3$	1461	1773	1071	—	—	—
$BaCo_3$	1437	1754	1059	—	—	—

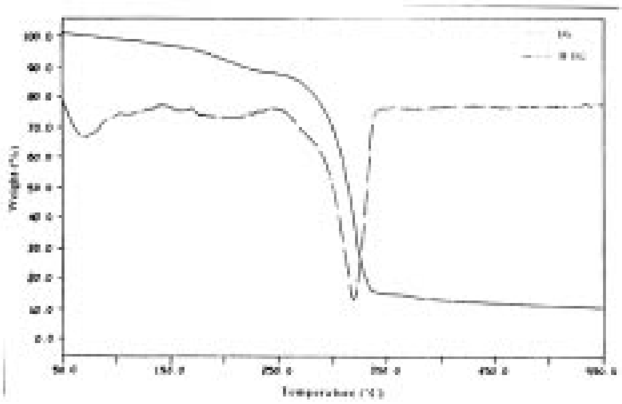

Figure 4
TG and DTG of Nickel palmitate (heating rate = 10 °C/min)

products (Table VII and Figure 4) except in case of silver palmitate that produces silver metal upon heating. This phenomenon may be taken place due to silver oxide transformation into silver metal upon heating at temperature higher than 600°C. X-ray diffraction of silver and silver palmitate were confirmed by appearance of their characteristic 'd' spacing published by ASTM cards N° 4-783 and 4-34 respectively (Figures 5,6 Table IV).

Table VII
Characterization of TG and DTG curves for transition element soaps

Metallic Soap	Thermal Step	Thermal Range	Loss%		Thermal Product
			Actual	Calculated	
$Mn(Pal)_2$	dehydration step	50-125	—		
	decomposition	>>500	6.96	7.53	Mn_2O_3
$Fe(Pal)_2$	dehydration step	50-186	—		
	decomposition	>>424.5	13	14	Fe_2O_3
$Ni(Pal)_2$	dehydration step	52-137	—		
	decomposition	>>500	12.7	13.11	NiO
$Cu(Pal)_2$	dehydration step	51.79-126.5	—		
	decomposition	>>450	12.6	13.8	CuO
$Zn(Pal)_2$	dehydration step	50.75-116.2	—		
	decomposition	>>483.25	12.6	14.1	ZnO
Ag-Pal	dehydration step	50.-116.2	—		
	decomposition	>>468.9	32.2	29.69	Ag

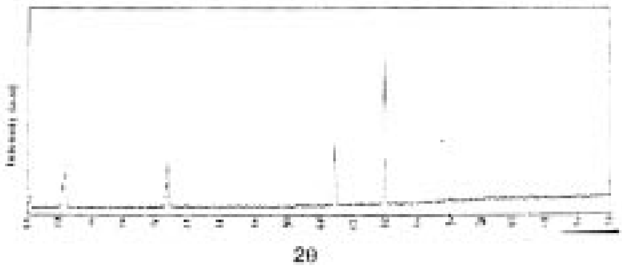

Figure 5
X-Ray diffraction pattern of Silver Metal

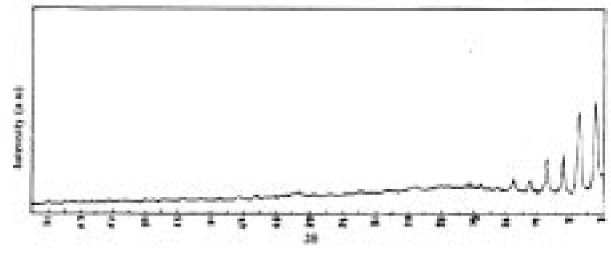

Figure 6
X-Ray diffraction pattern of Silver Palmitate

4. CONCLUSIONS

1. The thermal behavior of different types of palmitates is considered as an excellent guide before their use in different applications such as catalysts, and as fuel additives .

2. The palmitates of alkaline earth's specially of barium were found to be more stable than those of transition elements so that they can be used as lubricants due to their stability towards heating during manufacturing wire drawing .

REFERENCES

1. Werner,E . , Fritz,L. , Dieter, K. and Kurt, W.(1992). Preparation of metal 2,2- bis (hydroxymethyl) propionates as stabilizers of thermoplastic. Ger.Offen.D.E.4, 006,883, Appl 05Mar 1990; 6pp.- C.A. **116**, 20686 (Ger).
2. Linder,R.A and Koller, L.L (1997). Injection moldings from vinyl polymer containing lubricant and stabilizers. USA Patent, 13pp CODEN: $PIXXD_2$ PI: Wo 9611228 AI960418. AI Wo 95- US 12280 950922. PRAI US 94-320467 941007. C.A.**125**, 88165.
3. Chang, P.I.,Ray,C.D. and Gross, A.W.(1997). «Thermoplastics composition suitable for composting». Tredegar Industries,Inc., USA . U.S., 20pp CODEN: USXXAM. PI US 5258422A 931102. AI US 92-878738 920505. C.A.**120**, 136212.
4. Fredrick, S.S. and Hellmut, K.E. (1993). Fatty acids metals as non-phytotoxic fungicides with residual activity. (Neudorff,W.,G.m.b.H.K.-G.) PCT Int.Appl. Wo93 13,661,us Appl 818,613,10 Jan 1992; 34 pp. C.A.**119**, 111286.
5. Kirk, O. (1979). Encyclopedia of chemical technology, Third Edition. Awiley- Interscience Publication New.York. **8**, 43,44.
6. Demande, Fr. (1974). 2,213,973 (To Hardman& Holden Ltd).
7. Turner, J.H.W. (1974). 2,402,039 (To Hardman& Holden Ltd).
8. Ogawa, H. (1975). Additive for a Mineral Oil Especially for a heavy Oil. Japan 74 42, 886, Appl.67 83,735,27Dec 1967; 5pp. C.A.**82**, 158567.
9. Marwaha, S.B; Rubinstein, M.H. (1988). Structure-Lubricity evaluation of Magnesium Stearate. International-Journal-of-Pharmaceutics **43**, 249.
10. Anthony, V.C. (1988). Oils Spill Absorbent Material. U.S. Patent No.4, 780,518.
11. Arenase,A.S., Garcia, M.V., Redondo, M.I., Cheda, J.A.R, Roux, M.V. and Turrion,C. (1995) . Thermophysical study of lead (II) n-alkanoates by DSC,optiacl microscopy, FTIR and Raman spectroscopy. Liq.Cryst, **18**(3), 431-41.
12. Yasushi, K. and Ryohei, .M. (1961). Studies on the structure of Metal Soaps. Dep of Chem, Kyushu Univ Ser.**4**, No.1.
13. Redondo, M.I., Garcia, M.V., Gonzalez,T.M.J, and Cheda, J.A.R (1995). Spectroscopic study of phase transition of Cu^{+2} n-alkanoates. Spectrochimica . Acta, part A **51A**(3), 341-347.
14. Vold,R.D and Hattiangdi(1949) .Characterization of Heavy metals soaps by X- Ray Diffraction. Industrial and Engineering Chemistry **41**, 2311.
15. Annual Book of ASTM D- 4-829, 28-775, 6-520, 41-373,41-1442, 4-755, 5-664, 4-835, 5-661,4-783 and 4-34, Washington.
16. Robert C. W (1982). CRC Hand Book of Chemistry and Physics 62nd edition CRC Press, Inc . Boca Raton, Florida .

Recibido: Enero 2001
Aceptado: Junio 2001