

Abstract

The successful burning of heavy fuel in gas turbines depends on the additive to prevent hot corrosion of hot gas path components, to prevent vanadium hot corrosion in the turbine hot gas path, a minimum ratio of magnesium to vanadium is required.

In this work a number of oil-soluble and oil dispersible inhibitors were prepared to give a variety of magnesium complexes of different metal content and oil – solubility, these include;

1- Magnesium carboxylate which include : magnesium laurate, magnesium arachidate, magnesium palmitate, magnesium oleate, magnesium stearate, magnesium Cyclohexane carboxylate, magnesium benzoate, magnesium cinnamate, magnesium adipate, magnesium phthalate and magnesium terphthalate.

2- Magnesium sulfonate.

3- Water – Oil emulsion magnesium derivatives.

The emulsion were prepared following two routes;

a- by using sodium laural sulfonate as surfactant and magnesium chloride as magnesium salt.

b- by using magnesium sulfonate as surfactant and magnesium acetate as magnesium salt.

The prepared complexes were characterized by their FTIR spectra and their melting points.

The solubility tests show that the oleate complex of magnesium was found to have the highest oil solubility among the carboxylate derivatives.

The metal analysis, using atomic absorption spectroscopy, show the magnesium percent as follows :

Mg-arachidate < Mg-oleate < Mg-stearate < Mg-palmitate < Mg-laurate <

3.12% 3.52% 3.64% 4.17% 5.06%

Mg-cinnamate < Mg-benzoate < Mg-Cyclohexane carboxylate <

7.23% 8.39% 8.75%

Mg-phthalate < Mg-terphthalate < Mg-adipate

12.28% 12.33% 13.35

While the sulfonate derivative had (4.15 % Mg).

The magnesium percent of the emulsion prepared by rout (a) was (8.5 %) and that of rout (b) was (13.5 %).

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الخلاصة

يعتمد الاحتراق الناجح للوقود الثقيل في التوربينات الغازية على المضافات التي تمنع التآكل الحار (Hot corrosion) في أجزاء التوربين التي تتعرض لدفق الغازات الحارة، لمنع التآكل الناتج من الفناديوم (vanadium attack) الحاصل في الأجزاء الحارة من التوربين ، يتطلب ذلك استخدام اقل نسبة من المغنيسيوم لتكافئ الفناديوم الموجود في الوقود الثقيل.

تم تحضير مجموعة من معقدات المغنيسيوم في هذا العمل والتي تعطي ذوبانية متنوعة في الوقود ومحتوى فلزي مختلف، وقسمت إلى صنفين، المركبات الذائبة في الوقود، والمركبات العالقة في الوقود والتي تعمل كمانعات للتآكل. ضمت هذه المركبات مايلي :

١. كاربوكسيلات المغنيسيوم وشملت:

Magnesium laurate, Magnesium arachidate, Magnesium palmitate, Magnesium oleate, Magnesium stearate, Magnesium cyclohexane carboxylate, Magnesium benzoate, Magnesium cinnamate, Magnesium adipate, Magnesium phthalate and Magnesium terphthalate.

٢. سلفونات المغنيسيوم .

٣. مركبات المغنيسيوم المستحلبة (Water – Oil emulsion) ، حضرت هذه المستحلبات بإتباع مسلكين:

١. استخدام (sodium laural sulfonate) كمادة تساعد على الاستحلاب (surfactant) وكلوريد المغنيسيوم كملح.

ب. استخدام (magnesium sulfonate) كمادة تساعد على الاستحلاب (surfactant) واسيتات المغنيسيوم كملح.

شخصت المعقدات المحضرة باستخدام أطيف الأشعة تحت الحمراء ودرجات الانصهار.

أظهرت فحوصات الذوبانية ان معقد اوليت المغنيسيوم (magnesium oleate) هو الأكثر ذوبانية في الوقود من بين جميع الكربوكسيلات المحضرة .
اظهرتحليل المحتوى الفلزي باستخدام مطيافيه الامتصاص الذري ان نسبة المغنيسيوم تتبع التسلسل الاتي :

Mg-arachidate	<	Mg-oleate	<	Mg-stearate	<	Mg-palmitate	<	Mg-laurate
3.12%		3.52%		3.64%		4.17%		5.06%
Mg-cinnamate	<	Mg-benzoate	<	Mg-Cyclohexane carboxylate	<			
7.23%		8.39%		8.75%				
Mg-phthalate	<	Mg-terphthalate	<	Mg-adipate				
12.28%		12.33%		13.35				

بينما احتوى مشتق السلفونات على (4.15 % Mg)
أما نسبة المغنيسيوم في المستحلب المحضر بواسطة الطريق (أ) فكانت (8.5 %) بينما كانت في المسلك (ب) (13.5%)

السيرة الذاتية

الاسم الثلاثي واللقب : صلال عبد الهادي عبد الله المرهج .

التولد : ١٩٧٤ .

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موبايل : ٠٧٩٠٢٣٤٣٥٨٥

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2-1 Instrumentation:

1. Infrared spectrophotometer:

The IR of the prepared compounds was recorded using:

F.T.IR 8300 Fourier Transform Infrared Spectrophotometer
SHIMADZU, IN THE RANGE AT WAVE NUMBER (4000-400) CM^{-1} .

2. Atomic absorption spectrophotometer

PERKIN-ELMER Flame atomic absorption spectrophotometer, model 5000 (USA). Ca, Cu, Fe, Mg and Pb hollow cathode lamps were obtained from PERKIN-ELMER instruments.

3. Melting Points:

The melting points of the prepared compounds were obtained using **Gallenkamp** Melting Point Apparatus.

2.2 Chemicals:

2.2.1 Chemicals supplied:

Chemicals	Purity %	Company
Lauric acid		Fluka
Arachidic acid	99	BDH
Palmitic acid	99	BDH
Sodium Oleate	95	BDH
Sodium Stearate	98	BDH
Cyclohexane carboxylic acid	99	Fluka
Benzoic acid	95	BDH
Cinnamic acid	99	BDH
Adipic acid	90	Merk
Phthalic acid	90	BDH
Terphthalic acid	99	Fluka
Sodium hydroxide	99	BDH
Magnesium chloride six hydrate	95	BDH
Sulfonic acid		Commercial
Potassium hydroxide	99	BDH
Ethanol	95	BDH
Toluene	99	BDH
Benzene	99	Fluka
Carbon tetra chloride	99	BDH
Sodium laural sulfonate		Commercial
Magnesium acetate	99	Fluka
Xylene	99	BDH
Hydrochloric acid	Concentrated	BDH

2.3: Preparation of magnesium complexes:

2.3.1 Preparation of magnesium carboxylates:

0.0025 mole (0.1gm) of sodium hydroxide dissolved in 20 ml of distilled water was added to 0.0025 mole (0.5 gm) of the corresponding acid where all the acid was dissolved.

0.00125 mole (0.25gm) of magnesium chloride dissolved in 5.0 ml distilled water was added to the above solution or salt solution(in case oleate and stearate).The resulting precipitate, was filtered and washed with small amounts of water. The resulting complex was dried in vacuum for 6 hrs.

Table(2-1)show the types of base and acid (or it's salts)used in the preparation of the magnesium carboxylate.

Table(2-1) the types of base and acid (or it's salts)

Base	Acid (or it's salts)	Chemical structure
NaOH	<i>Lauric acid</i>	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
KOH	<i>Arachidic acid</i>	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
NaOH	<i>Palmitic acid</i>	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
-	<i>Sodium Oleate</i>	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COONa}$
-	<i>Sodium Stearate</i>	$\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$
NaOH	Cyclohexane carboxylic acid	$\text{C}_7\text{H}_{12}\text{O}_2$
NaOH	Benzoic acid	$\text{C}_7\text{H}_6\text{O}_2$
NaOH	Cinnamic acid	$\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$
NaOH	Adipic acid	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$
NaOH	Phthalic acid	$\text{C}_8\text{H}_6\text{O}_4$
NaOH	Terphthalic acid	$\text{C}_8\text{H}_6\text{O}_4$

2.3.2 Preparation of magnesium sulfonate:

1.0 gm of commercial sulfonic acid was converted to its sodium salt by addition of sodium hydroxide solution(10%) until the pH of the resulting solution became 7.00, and the brown color of original acid became light brown. To the resulting clear solution, saturated aqueous solution of magnesium chloride was added, then the solvent(water) was evaporated.

70.0 ml of (1:1)ethanol-carbon tetrachloride mixture was added to the residual precipitate, a light yellow solution was obtained and white precipitate of NaCl and excess MgCl₂ was separated. The solvent was evaporated until dryness, where yellow precipitate of magnesium sulfonate was obtained.

2.4 Test of solubility of magnesium complexes in different solvent

10.00 gm of magnesium complexes was dissolved in 100 ml hot solvent (benzene, toluene, and gas oil), the mixture was filtrated under vacuum at 25c°, the filtrate was dried in vacuum oven, the resulting solid mass was weighted to a constant weight.

2.5 Preparation of magnesium complexes as oil additives(stock solution) :

10.0 gm of soluble magnesium complex was mixed with heating and stirring with 50.0 ml fuel oil for 3hr.

2.6. Preparation of oil emulsion of magnesium

2.6.1 Preparation of oil emulsion of magnesium by using sodium laurel sulfonate

10.0ml saturated solution of magnesium chloride was mixed with 0.5gm sodium laurel sulfonate, the mixture was heating with stirring for 20 min. and then added to 50ml of crude oil, the mixture was heated and stirred for 1 hr. to complete emulsifying process.

2.6.2 Preparation of oil emulsion of magnesium by using magnesium sulfonate:

50% of magnesium acetate solution was added to 0.2 gm of magnesium sulfonate the mixture was added to 10 ml of crude oil, the mixture heated and stirred for 1 hr. to complete emulsifying process.

2.7 Determination of magnesium content in fuel additives:

2.7.1 Determination of magnesium content in the standard commercial additives.

5.0 ml of (10%) sodium hydroxide solution was added to 5.0 ml of standard commercial additive ,the mixture was stirred for 4 min. and then 10.0ml of xylene and 10.0ml of water were added to the above mixture and then heated for 30min, finally 20.0ml of conc. hydrochloric acid was added to the resulting and then stirred for 1hr. the two layers were separated using separating funnel and the magnesium content in the aqueous layer was determined using atomic absorption technique.

2.7.2 Determination of magnesium content in the prepared additives

2.7.2.1 Determination of magnesium content in magnesium carboxylate:

0.14gm of magnesium carboxylate was added to 5ml of xylene, to the resulting mixture 2.0ml of hydrochloric acid and 5.0ml of distilled water were added, then the mixture was shaken for 15min and left for 2hrs.

The aqueous layer was separated using separating funnel, the volume was completed to 25ml in a volumetric flask. A sample of this solution was analyzed for magnesium content using atomic absorption spectroscopy.

2.7.2.2 Determination of magnesium content in magnesium sulfonate:

0.3268 gm of magnesium sulfonate was dissolved in 2.0 ml of distilled water and, then the volume was completed to 25ml in a volumetric flask. A sample of this solution was analyzed for magnesium content using atomic absorption spectroscopy.

2.7.2.3 Determination of magnesium content in emulsion stock:

To 0.5 gm of emulsion solution (paragraph 2.5.2) ,10 ml ethanol was added, to the resulting solution 10.0ml of carbon tetrachloride was added, the resulting two layers were separated using separating funnel. to the aqueous layer 5ml conc. hydrochloric acid was added and the volume of this solution

was completed to 25 ml with distilled water in volumetric flask, in which the magnesium content was determined using atomic absorption technique.

1. Introduction:

1.1 Fuel

Fuel is any source of heat energy⁽¹⁾, it can be classified in three ways:
A-As solid, liquid, and gaseous depending upon their state of aggregation

e.g. Solid fuels: wood, peat, lignite, coals.

Liquid fuel : Petroleum fuels.

Gaseous fuel: natural gas.

B- Fuel can be classified as natural fuels and processed fuels

e.g. Natural fuels: wood, coal, petroleum, and natural gas.

Processed fuel: charcoal, kerosene oil, diesel oil.

C) Another classification distinguishes fuels as primary
and secondary e.g

Primary: coal, wood, and petroleum are used directly.

Secondary: are derived from primary fuel^(2,3,4).

1.1.1 Petroleum fuel:

The word of petroleum come from Latin words (Petra =rock and oleum =oil). It is a dark viscous liquid, found trapped in certain porous geological strata. The composition of petroleum is essentially a mixture of hydrocarbon of paraffin series, cycloparaffins and hydrocarbon of the aromatic series. The actual composition varies with the place of origin. It is classified as paraffin base if the crude oil remaining after the removal of volatile hydrocarbon is composed mainly of alkanes and as asphalt base if the residual crude oil is composed of cycloalkanes^(4,5).

Many series of hydrocarbon are found in petroleum, and table 1-1 refers to the hydrocarbon series found in petroleum⁽⁵⁾. Table 1-2 refers to the hydrocarbon found in typical light and typical heavy asphaltic crude

oil and the fuel components obtained by refining of a medium crude oil are show in table 1-3^(5,6)

Table 1-1 Hydrocarbon series found in petroleum⁽⁵⁾

No. of carbon atoms	Pennsylvania	Mid continent	California and Gulf coast
5	C_nH_{2n+2}	C_nH_{2n+2}	C_nH_{2n} and C_nH_{2n+2}
10	C_nH_{2n+2}	C_nH_{2n+2} and C_nH_{2n}	C_nH_{2n} and C_nH_{2n-6}
15	C_nH_{2n+2}	C_nH_{2n-2}	C_nH_{2n-2}
20	C_nH_{2n}	C_nH_{2n-4}	C_nH_{2n-4}
25	C_nH_{2n} and C_nH_{2n-2}	C_nH_{2n-4}	C_nH_{2n-4}
30	C_nH_{2n} and C_nH_{2n-4}	C_nH_{2n-8}	C_nH_{2n-8}
35	C_nH_{2n-4} and C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-12}
40	C_nH_{2n-4} and C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-12} and C_nH_{2n-16}
50	C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-16}
80	C_nH_{2n-8}	C_nH_{2n-16}	C_nH_{2n-20}

Table (1-2) Composition of Heavy and Light Crude Oil^(6,7)

	Percent of Total Crude	
	Light oil	Heavy oil
Normal paraffins (alkanes)	23.3	0.95
Branched chain alkanes	12.8	3.2
Cycloalkanes or naphthenes	41.0	19.2
Aromatic (mono-and Polly)	6.4	9.5
Naphtheno-aromatics or mixed	8.1	27.9
Hydrocarbons (include S compounds)		
Resins	8.4	23.1
Asphaltenes		16.5
Total	100	100

Table (1-3) Composition of Medium Crude Oil^(6,7)

	Carbon Number and Type	B.P. C°	Percent of Crude
Gasoline	C ₅ -C ₁₀ a, ia	180	25
Kerosene	C ₁₁ -C ₁₃ a, ia, ca, ar	180-250	10
Gas oil	C ₁₄ -C ₁₅ a, ia, ca, ar	250-300	15
Light oil distillate	C ₁₈ -C ₂₅ a, ia, ca, ar	300-400	20
Lube oil distillate	C ₂₆ -C ₃₅ a, ia, ca, ar	400-500	10
Residue (fuel oil, etc.)	C ₃₆ -C ₆₀ a, ia, ca, ar, r, as	500	20

a= alkanes, straight chain

ar= aromatics

ia= isoalkane, branched chain

r= resins

ca= cycloalkanes

as= asphaltenes

1.1.1.1 Heavy oil fuel

Heavy oil fuel is also known through other name, bunker fuel, resid, furnace oil and other often locally used names⁽⁴⁹⁾.

The origin of heavy oil (or bunker fuel) being considered is crude oil, when crude oil is subjected to refining, the lighter fractions (gasoline, kerosene, diesel, etc...) are removed by distillation. The heaviest materials in crude petroleum are not distilled, the boiling points are too high to be conveniently recovered. These materials (asphaltenes, waxes, and very large molecules) carry through refining and become residual (or resid). During various operations, in the refining (heating at high temperature), rearrangement of molecules many take place forming even large molecules materials that have still higher boiling points. These materials also become part of the resid. Finally, any contaminants in the crude will also be in the resid. This includes any salts (chemically elements that are typically soluble in water), sediment, and the heavy organic molecules from various sources.

The color of heavy oil fuel is always black, dark brown, or at least very dark. This color arises from the asphaltenes in the crude oil. Asphaltenes are very large molecules containing carbon, hydrogen, oxygen, sulfur, and some nitrogen⁽⁸⁾.

1.1.1.2 Heavy oil fuel contaminants

Any thing that doesn't distill during refining carries into the residual oil, this include not only water soluble metal salts sodium (Na), potassium (K), calcium (Ca), sulfates (SO₄) and several others, but also the oil soluble metals vanadium (V), lead (Pb), nickel (Ni) and others. Oil wetted materials such as rust and metal particles will also present. The water-soluble materials enter the refinery containing in very small droplets of

water dispersed through out the crude oil. As refining proceeds, the water is boiled away leaving the contaminants behind.

Sodium and potassium are contained in the water that is in fuel and could be washed out. Vanadium, nickel, and lead are oil soluble and cannot be removed from oil, therefore nearly all refiners simply concentrated the vanadium in the inexpensive resid fractions.

It is important to note that oil soluble metals vanadium and nickel are present as chemical molecules known as porphyrines. These come from the primordial materials that become petroleum. Porphyrines are very large molecules. As such they have very high boiling points. Therefore, they do not distill during refining. Because of the concentration effects when roughly 90% of each liter of crude is removed, these oil soluble contaminants are concentrated approximately 10 times in the resulting resid. Thus for a crude oil containing 15 ppm vanadium, the resulting resid would contain about 150 ppm vanadium.

The contaminant lead does not exist in nature as a crude oil contaminant. When found in oil or resids it is almost always due to fuel contaminant with lead gasoline.

Another contaminated in crude oil are sulfur. Sulfur exists as both a water-soluble contaminants such as contaminant metal sulfates, sulfites and sulfides and oil soluble contaminant such as polysulfides, thiols, mercaptans, and pyrroles. Except for adding to deposits in fired equipment^(8,49).

The common types of sulfur compounds are indicated in Fig(1-1)⁽⁵⁾ The percentage of sulfur contamination is proportionately higher, being generally between 0.5-3%. Chlorine contamination, generally from brine, can be as high as 2% .⁽⁶⁾

Other elements are present in smaller percentage and the nature and amount of these elements, determined by ash analysis, are given in table (1-4)⁽⁶⁾.

Table (1-5) refers to ash elements in heavy oil fuel that taken from some electrical powerstation in Iraq⁽⁹⁾.

Table (1-4)Ash Elements in Crude Oil in Part Per Million ⁽⁶⁾

Element	U.S.A	Venezuela	Colombia	East Indies	Middle East
Al	0.1-0.3	1	0.3	1.9-6	0.3-7
Ca	1.2-12	1.4	Nil	0.2	0.1
Cr	0.1	1.4	Nil	0.2	0.1
Co	1.6	Nil	Nil	1.9	Nil
Cu	0.2-0.5	0.2-7.3	7	0.4-1	0.1-5
Fe	3-4.6	1.2-3	0.4	15-64	1-5
Pb	0.2-0.7	Nil-2.1	Nil	0.6-0.7	Nil-0.1
Mg	0.5-2	0.6-1.7	1.2	0.8-1.7	0.1-7
Mn	Nil	Nil	Nil	trace	trace
Mo	Nil-0.1	Nil-0.3	Nil	0.2-0.6	Nil-0.2
Ni	0.8-1.2	0.3-6	10	0.4-1	0.4-0.3
K	Nil-2.9	Nil-2.1	Nil	Nil	Nil-0.7
Si	0.1-0.5	0.7-1.7	0.8	3.5-6.4	0.2-1.0
Na	2.7-38	13-33	9.4	6-15	0.1-0.5
Su	Nil-0.1	Nil-0.5	0.3	0.2-0.4	Nil
Ti	0.1-0.2	Nil-0.3	Nil	Trace-0.3	Nil-1-4
V	0.7-1.9	Nil-30	72	Nil	3-100
Zn	1.2-2.1	Nil-3	Nil	0.3-0.6	Nil-2

Table (1-5) Ash elements in heavy oil fuel taken from some electrical power stations in Iraq⁽⁹⁾.

PowerStation	V%	Ni%	Fe%	Cr%	Pb%	Mo%
Al-Musiab	29.8	5.4	2.7	8.23	1.9	0.04
South - Baghdad	21.6	8.0	106	6.5	3.3	0.06
Al-Dura	36.7	0.42	1.1	4.5	3.2	0.05
Beji	25.6	5.5	1.4	0.06	Nil	0.05

1.1.1.3 Melting points of material that occur in corrosive deposits

From the preceding analysis of solid and liquid fuel it is obvious that a whole range of oxides, sulphates, chloride, and possibly sulphides, could be deposited in both coal and oil fired plants. The nature of these deposits of particular importance because it appears that the presence of a liquid phase at the site of corrosion can produce accelerated corrosive attack.

Table (1-6-A) is a collection of previously published data and an attempt has been made to separate those deposits which may be particularly harmful in coal fired installations from those which are particularly relevant to fuel oil installations. ⁽⁷⁾

Table (1-6-A) Melting Points of Materials that Possibly occurring in Combustion Deposits (Oil and Coal).^(6,7)

Compound	Formula	Melting Point C°	Occurrence
Alumina	Al ₂ O ₃	2050	Possible in Both Coal and Oil - Fire Installation
Aluminum sulphate	Al ₂ (SO ₄) ₃	Decomp.770-Al ₂ O ₃	
Calcium oxide	CaO	2572	
Calcium sulphate	Ca SO ₄	1450	
Ferric oxide	Fe ₂ O ₃	1565	
Magnetite	Fe ₃ O ₃	1538	
Ferric sulphate	Fe ₃ (SO ₄) ₃	Decomp.480-Fe ₂ O ₃	
Magnesium oxide	MgO	2500	
Magnesium sulphate	Mg SO ₄	Decomp.1124-MgO	
Nickel oxide	NiO	2090	
Nickel sulphate	NiSO ₄	Decomp.840-NiO	
Silica	SiO ₂	1710	
Potassium sulphate	K ₂ SO ₄	1069	
Sodium sulphate	Na ₂ SO ₄	884	

Table (1-6-B) Melting Points of Materials that Possibly in Oil Combustion Deposits. ^(6,7)

Component	Formula	Melting point(C°)	Occurrence
Vanadium oxide	VO	2066	Most Important in oil fired installations
Vanadium trioxide	V ₂ O ₃	1970	
Vanadium tetraoxide	V ₂ O ₄	1970	
Vanadium pentoxide	V ₂ O ₅	675-690	
Sodium meta vanadate	Na ₂ O.V ₂ O ₅	630	
Sodium pyro vanadate	2Na ₂ O.V ₂ O ₅	640	
Sodium orthovanadate	3Na ₂ O.V ₂ O ₅	850	
Sodium vanadyl vanadntas	Na ₂ O.5V ₂ O ₅	625	
Sodium vanadyl vanadntas	5Na ₂ O.V ₂ O ₄ .11V ₂ O ₅	535	
Magnesium metavanadate	MgO.V ₂ O ₅	700	
Magnesium pyrovanadte	2MgO.V ₂ O ₅	835	
Magnesium orthovanadate	3MgO.V ₂ O ₅	1190	
Nickel pyrovanadate	2NiO.V ₂ O ₅	900	
Nickel orthovanadate	3NiO.V ₂ O ₅	900	
Ferric metavanadate	Fe ₂ O ₃ .V ₂ O ₅	860	
Ferric vanadate	Fe ₃ O ₄ .2V ₂ O ₅	855	

From Table (1-6-B) it well is seen that in coal fired plant the pyrosulphates and complex alkali iron sulphate are the most probable liquid phases present in the corrosive deposits. Where as with fuel oil firing, due to the very higher vanadium content generally present in the deposits, the most likely liquid phases are based on vanadium pentoxide

and sodium complexes. However, these are only general rules, and the actual deposits will depend upon the exact analysis of the fuel used ⁽⁶⁾.

1.2 Corrosion

Corrosion of metals may be defined broadly as the chemical action of their environment, often resulting in their deterioration or destruction. It occurs because in mainly environments most metals are not inherently stable and tend to revert to some more stable combination of which the metallic ores, as found in nature, are familiar examples. Under most ordinary conditions of exposure the corrosion products consist mainly of oxides, carbonate, and sulphides⁽¹⁰⁾.

At high temperatures the product may be largely made up of oxide. Ash fouling and corrosion are major problems when burning heavy oils. Ash deposits jeopardize heat transfer to metallic surfaces and cause corrosion of the combustion hardware, thus decreasing its lifetime ^(11,12). The flame-side corrosion of metal surface, together with heat transfer surface fouling is the main problem at heavy fuel oil combustion. There are several critical regions in steam boilers, where the corrosion from the flue gas side could proceed. The corrosion intensity is influenced by the following factors⁽¹³⁾.

A-Oil composition especially by the content of inorganic substances such as V, S and alkali metals.

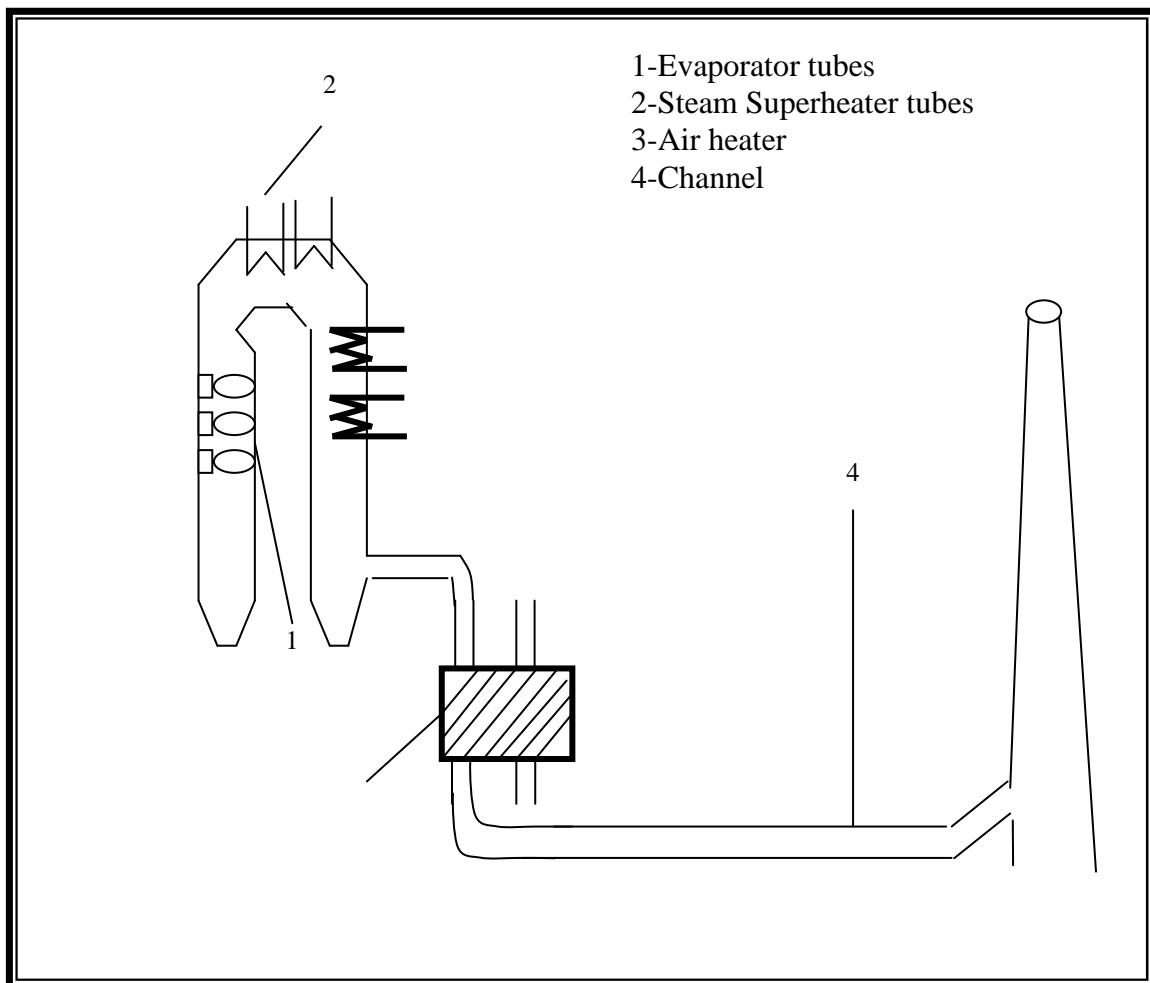
B-Combustion air excess ratio and predominantly gas composition on the tube/gas interface.

C-Temperature of metal/ deposit layer interface, which determines the occurrence of the following liquid phases:

1- Molten and semi-molten layer deposits at high temperature boiler region.

2- Concentrated sulphuric acid in the low temperature boiler region.

The critical regions are illustrated schematically in fig.(1-1)⁽¹³⁾ and each of them is distinguished by the different corrosion mechanism as reviewed in table (1-7)⁽¹³⁾.



Figure(1-1):Critical Corrosion Regions in the Oil-Fired Steam Boiler ⁽¹²⁾

Table (1-7):Critical Corrosion Regions in the Steam Boiler and their Limiting Factors⁽¹²⁾.

No.	Corrosion region heat transfer surface	Limiting factor		Corrosion mechanism
		Gas/Deposit Composition	Temperature C°	
1-	Evaporator tubes	100vpm H ₂ S	> 280	Hot gas corrosion
2-a	Superheater tubes	Molten sulphates	> 620	Sulphate/sulphite corrosion
2-b	Superheater tubes holder	Molten vanadates	550-600	Vanadic corrosion
3-	Air heater	H ₂ SO ₄ /liquid	100-140	Low temperature corrosion
4-	Flue gas channel	Acid deposits	Dew point	

The ash stems from the inorganic content of the fuel. Where the origin of these constituents is varied:

- (a)- The animal and vegetable sources from which the oil was formed.
- (b)- Contact of the oil with the underground rock structure.
- (c)- Production, storage, handling and transportation facilities.

In general, inorganic components concentrate in the asphaltic constituents of residual oils to a typical maximum concentration 0.2%⁽¹²⁻¹⁵⁾.

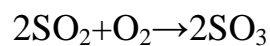
1.2.1 Cold-End Corrosion (Sulfidation Attack)

In the case of the cold-end the offending element is sulfur. Sulfur occurs naturally in the crude oils that are refined. The level of sulfur is concentrated into the residual fraction and finds its way into nearly all boiler fuels at varying levels. The level encountered is normally related to the specification level of the fuel purchase contracts. When sulfur is burned in the presence of oxygen (required to support combustion) it forms sulfur dioxide. Normally about 1 - 2% of the sulfur dioxide is further reacted with additional oxygen to form sulfur trioxide. More or less may be formed based upon the conditions found in the boiler. For example levels of excess air/oxygen (higher, more formed); vanadium, nickel or iron (higher, more formed); sulfur in the fuel (more present, more formed); size of boiler (larger, more formed); temperature of firebox (higher, less formed); and the residence time in the boiler (longer, more formed). All of these factors are competing at the same time making prediction of the actual amount of sulfur trioxide that will be formed difficult. The following table(1-8) shows the expected amount of sulfur trioxide based upon excess oxygen and sulfur content⁽¹⁶⁾.

Table (1-8) Estimate of sulfur trioxide in combustion gas(ppm)⁽¹⁶⁾

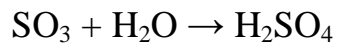
% Sulfur in fuel	0.5	1.0	2.0	3.0	4.0	5.0
Excess O ₂ %	OIL FIRED UNITS Sulfur Trioxide Expected in Gas (ppm - parts per million)					
1	2	3	3	4	5	5
2	6	7	8	10	12	14
3	10	13	15	19	22	25
4	12	15	18	22	26	30

The chemical reactions forming these sulfur compounds are represented as follows : $S + O_2 \rightarrow SO_2$



One interesting note about the second reaction in particular is that the presence of hot iron surfaces and vanadium slags are required to make the reaction go in the direction indicated. If there were no surfaces to actively catalyze this reaction, the temperatures found in boilers would effectively limit the formation of sulfur trioxide by forcing the reaction in the reverse direction. Sulfuric acid can no longer be formed so there is no acid plume. The formation of sulfur dioxide or trioxide is not a problem within the boiler (although this can be a problem outside the boiler when in the atmosphere - acid rain). The problem with sulfur trioxide is that it condenses with water vapor (formed from the combustion of hydrocarbons in the presence oxygen)

to form sulfuric acid according to the following reaction



(Sulfur dioxide has a similar reaction, but the resulting acid normally does not condense at boiler temperatures.)

The formation of sulfuric acid is a problem because when temperatures are low enough, the acid can condense on metal surfaces causing a severe corrosion problem. This cold-end corrosion normally occurs in air preheaters where temperatures can be low enough - after heat is removed to warm incoming air - so that the acid condenses on the metal surfaces. Sulfuric acid corrosion can also occur on stack walls and particularly on any metal tops of stacks leave a stack are particles of fly ash with adsorbed acid on them. When these smuts float to the ground and deposit on automobiles, they can cause additional problems⁽¹⁷⁾.

1-2-2 Vanadium Attack (High Temperature Corrosion)

Vanadic attack was first observed in the early 1940's in naval ships burning residual fuel oils⁽¹⁸⁾. Vanadium is a common fuel contaminant in "black" oils. When these fuels are combusted, vanadium forms (primarily) vanadium pentoxide (V₂O₅). Vanadium pentoxide melts about 675 °C. When it is molten, vanadium pentoxide behaves as an excellent solvent for the metal oxides that high temperature alloys form to protect their surfaces. When in a molten state and while a solvent, vanadium pentoxide strips away these oxides. The metal surface atoms respond by forming a new layer of oxide coating which is again stripped away. As the process continues, the metal surface undergoes corrosion as each successive layer is stripped away⁽¹⁹⁾.

Vanadium appears in fuel in the form of oil-soluble porphyrins. These organic vanadium compounds decompose in the gas stream to give mainly (V₂O₅). Vanadium pentoxide is most damaging since due to its low melting point (690°C) it is in its liquid state at normal combustion temperature.⁽¹⁸⁾

It has been mentioned that in residual fuel oil deposits vanadium oxides can be a major constituent.

The type of attack has been suggested to occur by three mechanisms appear to be possible⁽²⁰⁾ :-

A .The vanadium compounds act as a carrier for oxygen.

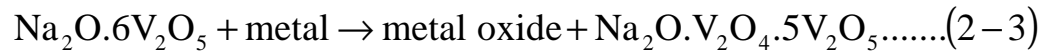
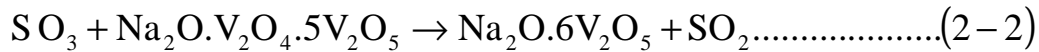
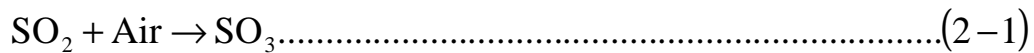
B .The vanadium compounds dissolve the oxide scale.

C .Vanadium enters the oxide scale on the metal, increase the defect mechanisms and allowing accelerated attack.

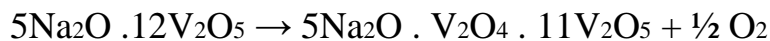
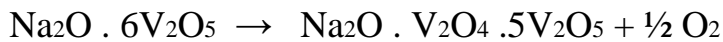
However, it is generally observed in accordance with most studies on corrosion by deposited salts, that accelerated attack occur only when a molten phase is present as was reported by Amgwe et al⁽²¹⁾ .The attack was found to increase with temperature, time of immersion and amount of ash present. They proposed that the liquid vanadium compounds destroyed the scale and acted as oxygen carriers and supported their conclusions by showing that in an atmosphere of nitrogen accelerated attack was no longer observed. Thus, of the proposed mechanisms, A and B appear reasonable whilst C receives little support.⁽²²⁾

As the presence of a liquid phase in promoting accelerated attack is so important and as the principal ash constituents of low-sulphur-high vanadium fuels contain the oxides of sodium and vanadium, the melting points of the various compounds formed are important. These have already been shown in Fig.(1-2), where it can be seen that a series of compounds are formed between (Na_2O) and (V_2O_5) , some of which have melting points below the operating temperature of boilers and turbines. The eutectic formed between ($5\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$) and sodium metavanadate ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$) melts at (527°C) and most of the compounds between (V_2O_5) and (Na_2O) melt below (675°C). However, under an atmosphere containing oxides of sulphur, other components can form in an analysis of the ($\text{Na}_2\text{O} - \text{V}_2\text{O}_5 - \text{SO}_2 - \text{O}_2$) system, (e.g. Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_7$, $\text{V}_2\text{O}_5 \cdot 2\text{SO}_3$ and $\text{V}_2\text{O}_5 \cdot 1/2 \text{SO}_3$).

The oxygen – carrier mechanism is postulated as:-



or



A liberation of atomic oxygen takes place at the moment of solidification. This oxygen loosens up the whole melting cake by forming bubbles and attacks the metal surface. During the melting process the oxygen is absorbed again from the surrounding exhaust gas. The sodium vanadyl- vanadates thus act as an oxygen transmitter (oxygen pump) and transports the oxygen to the metal surface during the processes of melting and solidifying at a temperature range of 530 - 600 °C⁽⁵²⁾.

The iron oxide formed in this process - nickel oxide in case of Cr-Ni steel - diffuses in the melting cake.

The result is an uninhibited attack of corrosion on the metal surfaces which are exposed to the described temperature range. In heavy fuel engines the parts specially concerned are outlet valves, piston crowns, nozzle rings and blades of the turbo charger. The process of the slag deposits and the temporary corrosion attack on the engine components partly depend on the total content of ash-forming elements and partly on the ratio they have amongst themselves. Considering the melting behaviors mentioned above and the examinations of diesel engine outlet valves, a Na/V-mass ratio between 0.08 and 0.45 is especially dangerous.

The range of the strongest corrosion corresponds to a Na/V-mass ratio of 0.15 to 0.30. These and further examinations on the temperature dependant corrosion of iron and chromium-nickel steels of different composition allow

two main conclusions to be drawn:

1-The ratio of Na_2O : V_2O_5 and of Na : V has a decisive influence on the melting behavior of slag.

2-The temperature of the components of an engine operated with heavy fuel decisively determines the corrosion intensity.

Measurements at the outlet valves of diesel engines and at pistons confirm this finding^(53,23).

The degree of corrosion is dependent on the composition of the fuels, on the material used, on the O_2 contents of the exhaust gas and on the local temperatures⁽²³⁾.

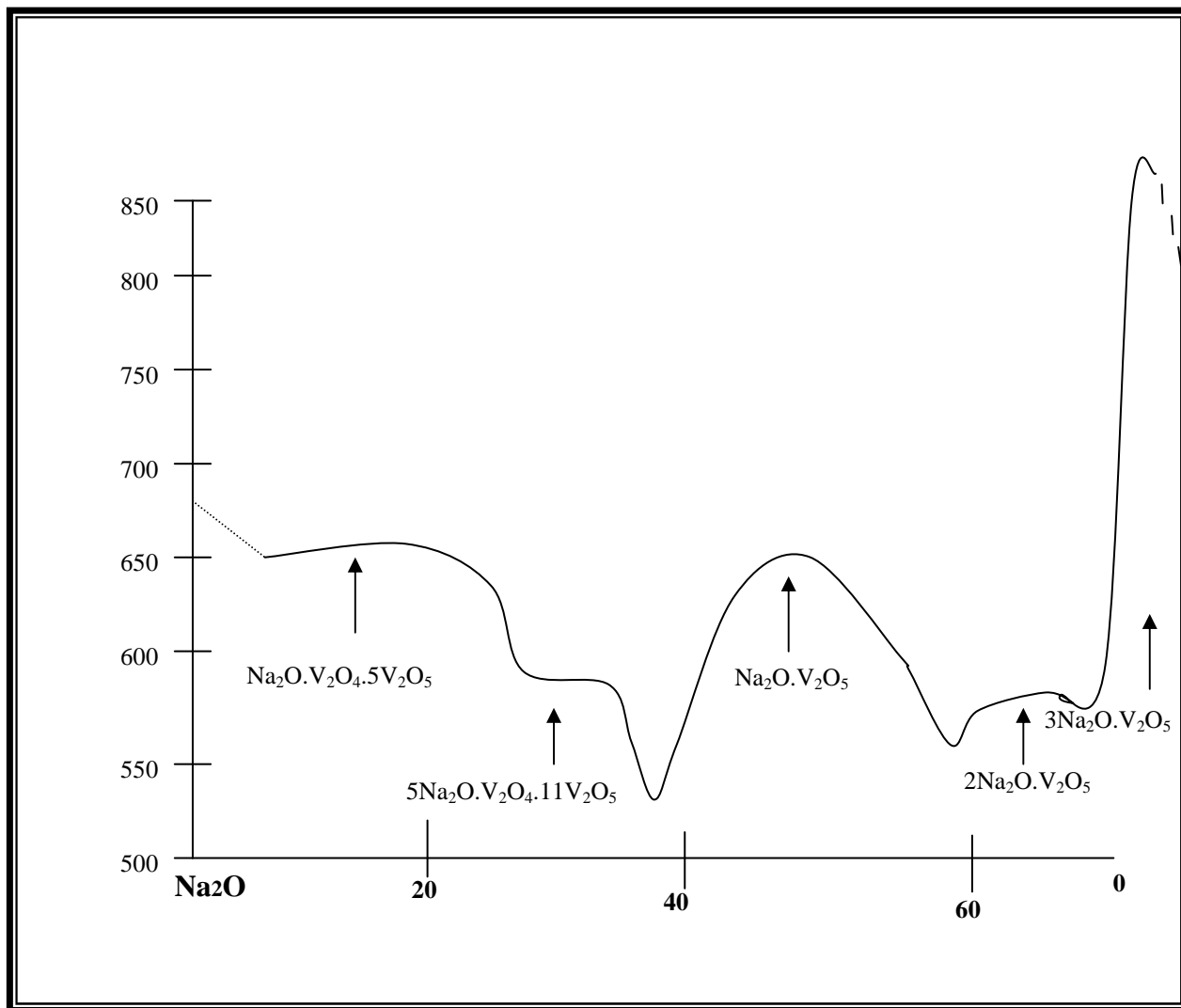


Fig. (1-2) Vanadium Pentoxide-Sodium Oxide Melting Point Diagram^(22,23)

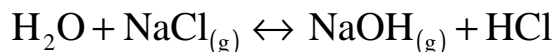
1-2-3 Slag Formation

Slag formation from vanadium, sodium, sulfur, oxygen, and other metals such as nickel is a more widespread problem associated with contaminated fuels than is corrosion. In this slag problem, the above metals (and others) form various metal oxides and sulfates when combusted. These materials typically have melting points above typical boiler operating temperatures. Also combinations of these oxides and sulfates form eutectic mixtures that have even lower melting points than the “pure compounds.” While molten these materials are sticky. They collect on the cooler boiler water tubes and solidify. However, the outer surface is still hot and sticky which collects additional deposits. As the deposit grows the inner “rings” cool and continue to build thickness. This cycle can form very thick deposits in many cases. These insulating deposits interfere with the efficient transfer of heat from the fuel combustion into the water tubes to boil water. The boiler operator is forced to increase his fuel consumption rate to compensate for the loss of heat transfer. As less heat is transferred into the tubes, it just passes through the boiler and ultimately out the stack. In effect, the money spent on fuel is just going up the stack^(24,52).

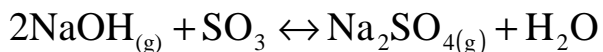
1-2-4 The Na₂SO₄ Attack

Damage is generally associated with the combined presence of vanadium (arising as a porphrin in the fuel), sodium (derived from sodium chloride), sulphur (from the fuel) and oxygen. During combustion, vanadic oxides and sodium sulphate may condense as low as melting vanadyl vanadates, which permit the rapid dissolution of surface oxides and metal alkali, The processes occur very rapidly. Oxide dissolution can appear to be synonymous with metallic loss⁽²⁵⁾ .

It is covenant to discuss the roles of sodium and sulfur together since it is the compound (Na₂SO₄) which is involved in the hot corrosion reaction. The sodium in the oil is mainly present as (NaCl) and is readily vaporized during the combustion process.⁽²⁶⁾ There are a number of different mechanisms by which vaporization can takes place, but once complete, most of the sodium exist in the vapor phase as either (NaCl) or (NaOH), their proportions being determined by interactions of the type:-

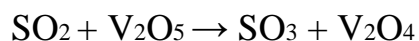


(SO₃) in the flue gases will react with this (NaOH) to form (Na₂SO₄) which will condenses as such :-

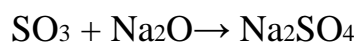


Sulfate formation becomes increasingly favorable thermody- namicly, as the temperature decreases. The presence of sodium sulfate increase the oxidation rate.

The SO₂ present in the exhaust gas also has an influence on the high-temperature corrosion. It is bound by Na₂O/V₂O₅ melting according to



and



and is found in all melting layers. Sodium sulphate once formed can however not exist in melting of sodium vanadates and is set free, so it can also attack the surface of materials. In addition sulphurous acid SO_3 in a sulphurous deposit has the tendency to dissolve oxides so that protecting oxide layers are destroyed.

Electro-chemical examinations according to show that sulphates cause an increase in corrosion at temperatures above 600°C which again is considerably increased when vanadylvanadates are present⁽¹⁹⁾.

1.2.5 Hot Corrosion Mechanisms

The presence of a liquid phase on the surface of a metal is usually necessary for corrosion reactions to occur high rates. The presence of ionically conducting sulphate melts can transfer electrons from anode cathode as shown in Fig.(1-3) .Areas of metal covered with molten sulphates are move anodic then areas beneath solid deposits⁽²⁷⁾.Metal wastage on boiler tubes is greatest at the sides rather than directly in line with on coming gas stream, where the deposit is thickest Alkali-sulphates also corrode metal surfaces by reacting with the iron oxide protecting layer. Examination of tube deposits from operating furnaces frequently shows a higher content of alkali metals in the inner layers of deposits then in the outer layers. There seems to be a migration of alkali metals to the cooler inner layer.^(28, 29) .

Vanadic oxides attack the metal surface by dissolving the normally protective oxide layer and assisting in the transport of oxygen to the pure metal surface.⁽²⁸⁾

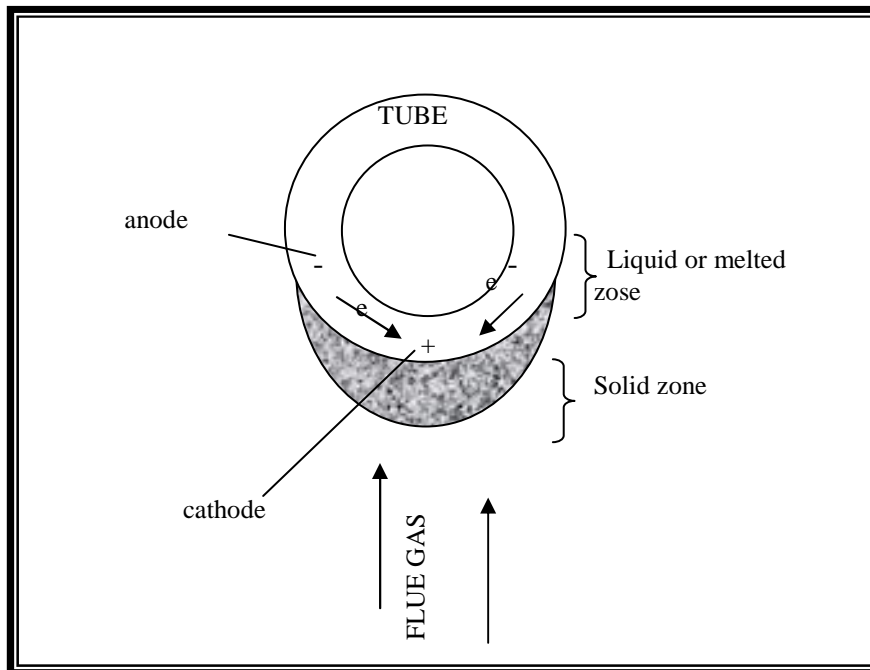


Figure (1-3) Mechanism of Hot Corrosion⁽³⁰⁾

1.2.6 Mechanisms of Deposition.

Deposits accumulate on a surface by at least four physical processes⁽²⁸⁾.

- 1-**Molecular diffusion, particles less than 100nm behave like gas molecules.
- 2-**Brownian motion, particles between 0.1-1 micrometer have a random-walk path when “pushed “ by gas molecules.
- 3-**Turbulent diffusion, particles between 1-10 micrometers enter the turbulent region directly over a surface, pick up kinetic energy from the gas eddies and there by are able to move through the laminar part of the boundary layer to the surface.

4-Initial imprecation, particles over 10 micrometers which receive sufficient kinetic energy from the main gas stream penetrate a boundary layer or a turbulent region, or follow a straight path independent of the gas flow turning “corner”.

The Fig.(1-4) shows the deposition rate of particles in a boiler furnace with mean gas velocity of 30m/s . Particles with the size of between (0.1-1) micrometer are the less likely to be deposited.⁽³¹⁾

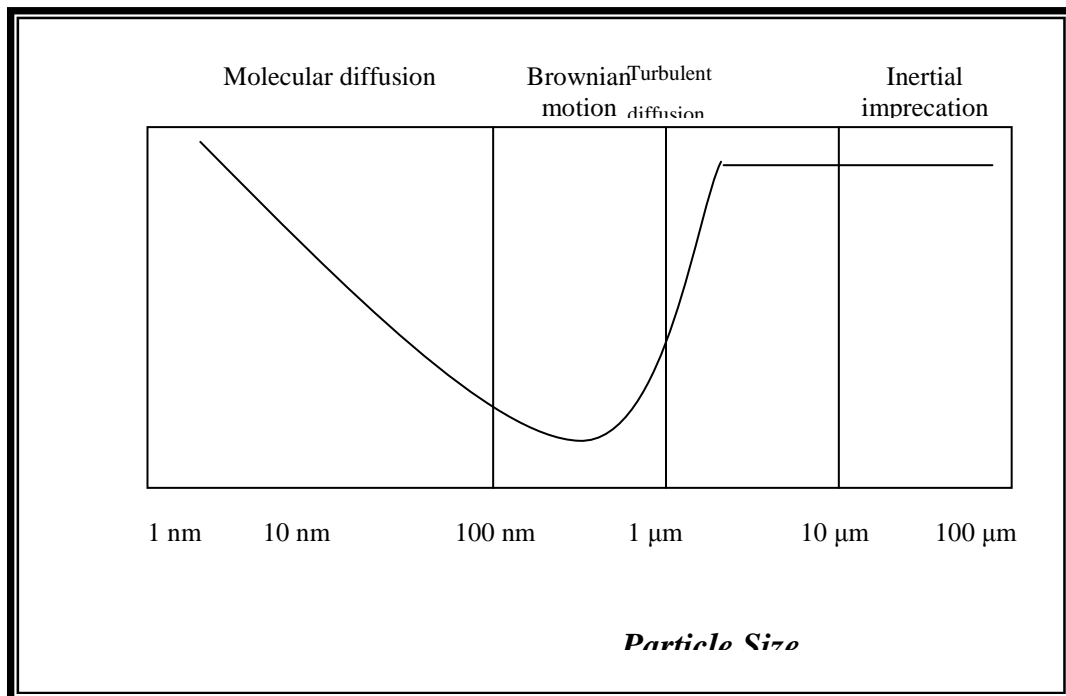


Figure.(1-4) Deposition Rate of Particles in a Boiler Furnace⁽²⁸⁾.

Deposit accumulation of ash to form massive deposits will not only depend on the size of the particles but also on the adherence of stickiness of particle. Sodium and potassium play an important parting inducing sintering. They form low-melting compounds with silicates, vanadium and lower temperature eutectics with for instance (CaSO_4 , MgSO_4) In the flame with high temperature and turbulence, liquid droplets can capture

other particles, large enough so that they caught by a surface through inertial impact liquid phase is more likely to ensure a adherence to a solid surface. Some particles (ex. SiO₂) although not molten, may have a highly viscous surface.⁽²⁸⁾ .

1.3 Solutions Of Chemical Problems

It is impossible to prevent some degree of interaction between a metallic component and high temperature gases so the common term “prevention” is not strictly applicable. What is meant is a reduction of the interaction to a very low value. There are many ways by which this could be attempted in contaminated combustion atmospheres and the approaches used depend upon either (1) changing the environmental conditions or (2) changing the material .

There are three basic ways in which the environmental conditions can be modified to reduce the corrosion problems and these are:-

A . Fuel washing

B . Addition of corrosion inhibitors

C .Changing the combustion condition to minimize attack⁽³²⁾ .

Fuel washing is followed to remove the water-soluble contaminants sodium and potassium and the subsequent addition of a magnesium additive to inhibit the effects of vanadium and lead⁽³³⁾. Table (1-9)show the water soluble and oil soluble species .

Table (1-9) Water Soluble and Oil Soluble Harmful Species

Water Soluble	Oil Soluble
Sodium	Vanadium
Potassium	Lead
Calcium ...etc.	Nickel... etc.

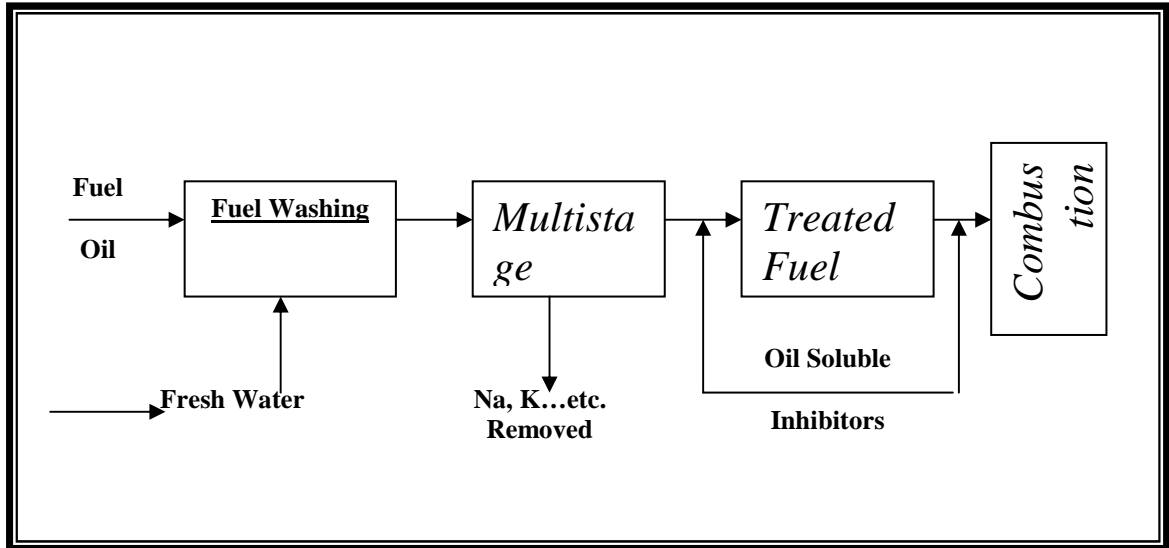
1.3.1 Fuel Washing

The principle of fuel washing is to mix into the fuel "clean water" and then remove the water. The water-soluble sodium and potassium are removed with the water. Sodium and potassium arise from salts (typically sodium chloride - the salt in salt water - and potassium chloride) that are contained in the crude oil as it is pumped from the ground. Thus the only way sodium and potassium can exist in the fuel is to be present in water droplets. It is important to realize the sodium and potassium are very concentrated in the droplets of water. It is not uncommon to have the concentration be above 2000 ppm of both elements in the water droplets. Thus for a resid that contains 1% water and sodium plus potassium of 40 ppm, the water droplets would contain $40/0.01 = 4000$ ppm in the water droplets. These are important points to remember, fuel washing relies on these principles.

To remove the sodium and potassium it then becomes a "simple" matter or adding a quantity of sufficiently pure water, mix it

thoroughly into the fuel to contact the water droplets in the fuel to dilute the concentration of sodium and potassium in the water droplets, and then to remove as much of the water as possible⁽³⁴⁾.

Fig(1-5)illustrated the washing steps.



Figure(1-5) The Fuel Washing with Water and treatment of fuel⁽³⁵⁾

1.3.2 metals used to control high temperature corrosion by fuel

additives:

Fuel additives which are formulated to control high temperature corrosion ,were designed to address particular contaminant situation and operating condition. All of them based on the following active component and may offered in combination and concentration : magnesium ,chromium, silicon, iron and manganese.

Additives containing magnesium are used primarily control vanadic oxidation through combination with V_2O_5 at an appropriate Mg /V treatment ratio, magnesium orthovanadate [$3MgO.V_2O_5$] with a high

melting point of about 1243c° is formed as a new ash component. Chromium additives are specially designed to inhibit sulfidation corrosion promoted by alkali metals contaminants such as sodium and potassium, chromium has also been shown to reduce ash fouling, and the mechanism is believed to involve the formation of volatile compounds which pass through the turbine without depositing.

Additives containing silicon are also used to provide added corrosion protection and improved ash friability in specific application⁽³⁶⁾.

Oil-soluble iron compound in the form of salts of aliphatic carboxylic acid were used as additives for improving the combustion of liquid fuels, and the other side iron oxide dispersion is also used in this respect. The dispersion product reached maximum smoke reduction at 55 ppm iron as compared with an oil soluble product that reached a maximum reduction at 30 ppm iron.

This may be attributable to the difference between level with dispersion having an average particle size of 0.5 to 1.0 micrometer⁽³⁷⁾.

1.3.3 Magnesium Additives as a Corrosion Inhibitors

Early in the development (1950's) of gas turbines the corrosive effects of vanadium were noted. Many gas turbine manufacturers embarked on research programs to discover a solution to the corrosiveness of vanadium. As a result of all this work, one metal stood out as the most economical and effective of those tested magnesium⁽³⁸⁾.

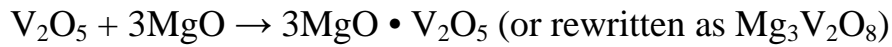
The minimum treating ratio of three parts of magnesium to one part of vanadium was determined to be correct in the late 1960's to early

1970's. Initially the treat rate was set at 3.5 to 1 to insure adequate magnesium would be added. The more appropriate 3:1 was agreed upon as an industry standard since the early 1980's. The actual stoichiometric amount of magnesium required to just react with vanadium to make safe compounds is only about 0.7:1. However, additional magnesium is added because not only is the desired magnesium orthovanadate formed, but other less desirable magnesium vanadium compounds are also made. To force the reaction to the desired product, more magnesium is required. Other magnesium products are also formed (magnesium oxide and magnesium sulfate). More magnesium needs to be added to offset these less desirable compounds. And finally, since the time allowed for the reaction is very short (high gas velocity in the region of the flame), the greater the amount of magnesium added, the greater are the opportunity for a vanadium atom to find a magnesium atom⁽³⁹⁾.

Most if not all gas turbine locations that use additives have selected either type sulfonates or carboxylates. Oil soluble additives, although sometimes more expensive to use than water solutions are much more convenient to use so that most users have decided the cost savings are not important. Another advantage of oil soluble products is they are delivered to the user ready to be used. With water solutions it is necessary to batch dilute the crystals and to either take a chance on the concentration, do an analysis, or treat with higher levels than needed to be on the safe side. Using more additive than required reduces any cost advantage the water-soluble products may have⁽⁵¹⁾.

No matter the source of magnesium, the mechanism to solve vanadium corrosion is the same: raise the melting point of vanadium pentoxide to one above the gas turbine temperatures. By adding

magnesium, vanadium orthovanadate is formed instead of vanadium pentoxide. This reaction is reproduced below:



Magnesium orthovanadate melts above 1200C°. This temperature is well above typical gas turbine temperatures, especially blade temperatures due to blade cooling. When the system temperature is lower than the melting point of a compound, the compound (magnesium orthovanadate in this case) is not melted, it is a solid. Thus magnesium orthovanadate is solid in the gas turbine. Vanadium pentoxide is only corrosive while it is molten. When converted to the orthovanadate (in the flame) it will pass harmlessly through the system. Thus by adding the appropriate quantity of magnesium (3:1) the system will be protected from corrosion. This has been the case for well over 25 years of magnesium use in gas turbine applications using heavy fuels.

The extra weight resulting from using magnesium additives causes a loss of power every 200 hours of operation⁽³⁸⁾.

1.3.3.1 Form of Magnesium Additives

Magnesium has been used because it has a relatively low atomic weight that means that more atoms of magnesium can be added to fuel for a given weight of additive. And since magnesium is relatively plentiful and easy to obtain from nature, the cost can be bearable for this application. Magnesium is

magnesium; the reactions discussed will occur no matter the source of the magnesium. What is different is the nature of the products, their reactivity and the manner in which the products are used. The following is a quick summary of the different types of magnesium products that have been used over the years⁽¹⁷⁾.

A. Powders

Powders are typically magnesium oxide or hydroxide. Particle sizes range from a couple of microns up to tens of microns. The concentration of magnesium in powders is the highest of any magnesium products with magnesium oxide being 60% magnesium. Powders are very inexpensive. Handling problems make powders less than desirable to use. The inclusion of any moisture in a powder will cause clumping. For this reason it is necessary to keep sacks of powders dry. It may also be necessary to break up the powder particles before addition so their size is more uniform⁽⁵⁴⁾. Powders are often added to the back end of a boiler between the superheater and the economizer. They cannot be added to the fuel since they are insoluble and would separate from fuel if the fuel were not kept in motion. Erosion of valves and burner tips could also result if a powder were added to fuel. Magnesium hydroxide is more reactive than magnesium oxide. When the hydroxide is added to the hot furnace (or flame) it converts to magnesium oxide at that point and thus is more reactive. Many magnesium oxide powders are "dead-burned" which means they have been heated to high temperatures during drying..so..theyareno..longer..reactive⁽⁴⁰⁾.

B. Slurries

Slurries are generally magnesium oxide or hydroxide powders dispersed in a light fuel oil . A dispersing aid is included to stabilize the powder in the slurry. Particle size is generally down to around 1 micron. The smaller the particle size, the more expensive the slurry. Slurries are normally added to the fuel line just before the burners since they are not truly soluble in the fuel. This minimizes the

1.3.4 Combustion Control

A great deal can be done to minimize corrosion problems by details in boilers and turbines. Obvious points such as avoiding direct impingement of the flame on superheated tubes and design of burners to give uniform conditions throughout the installation can overcome localized problems.⁽⁴³⁾

Oil droplets burn by stages and droplet size can effect the corrosive products produce, e.g. coarse atomization has been shown to be advantageous in reducing deposition from high vanadium fuels.⁽⁴⁴⁾ It is claimed that the increased carbonaceous matter in the larger droplet reduces the oxide of vanadium so that they pass through the turbines rig as the high melting point (V_2O_3) and (V_2O_4) and this causes reduction in deposition and corrosion⁽⁴⁵⁾.

Zwillenberg⁽⁴⁶⁾ studied the use of water-in-oil emulsions (in which each fuel droplet leaving the atomizer contains a number of microdroplets of water) is a promising technique, which has been proposed for the reduction of smoke and (NO_x) emissions from boilers and gas turbines. Other possible benefits include:

A . The reduction in excess air with consequent reduction in SO_3 formation.

B . The elimination of metal-containing antismoke additives and the resulting deposits and fouling in gas turbines,

C . The ability to use heavier and cheaper fuel.

Fig.(1-6) shows some of the systems discussed at a symposium⁽⁴⁷⁾ on “water-in-fuel emulsions” and Fig. (1-7) shows the microexplosion phenomenon⁽⁴⁷⁾.

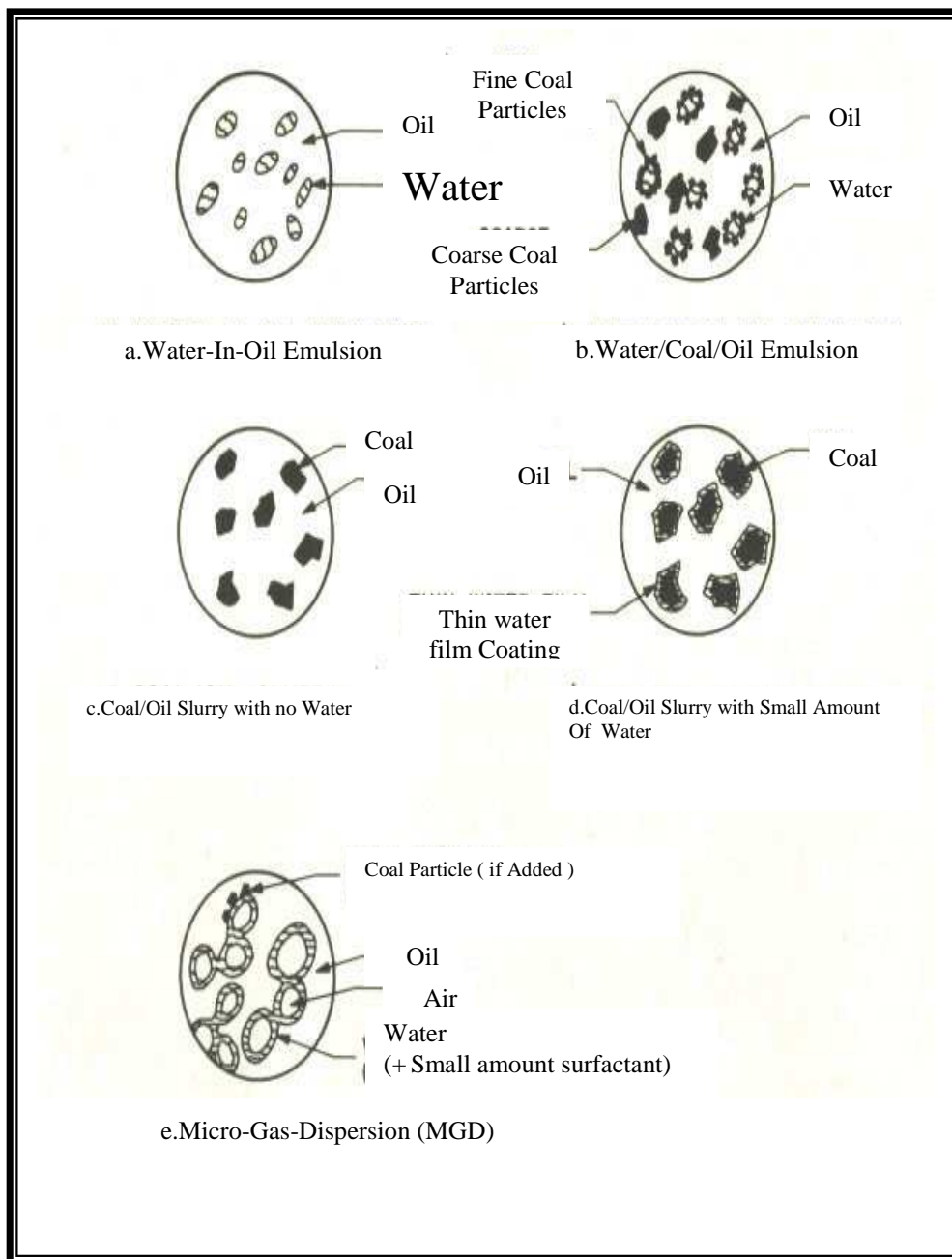


Figure (1-6) Types of “Emulsions” Discussed at Symposium on the Use of Processes, U.S. Dot, Cambridge, Mass⁽⁴⁷⁾.

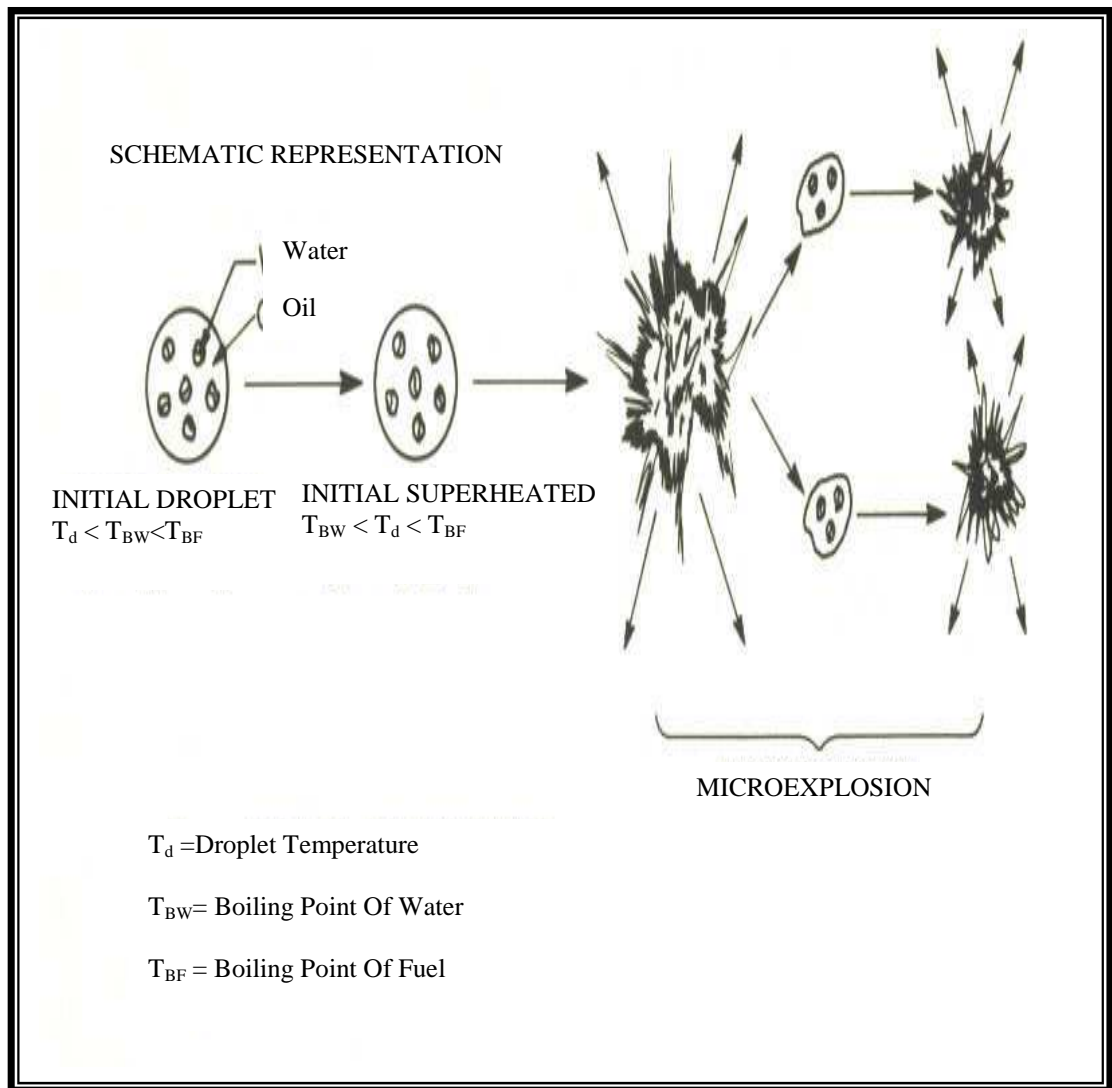


Figure (1-7) Mechanism of Emulsion Combustion Illustrating “Microexplosions”⁽⁴⁷⁾

1.3.5 Surface coatings

Oxide scales build up a protective layer on the metal surface ,separating the substrate from the corrosion environment. Coatings provide active elements for building-up this protective oxide scale. The use of corrosion resistance coatings for existing alloys has found widest application in the gas turbine and boiler field. Metallic coating has been applied by electrodeposition, high temperature diffusion and plasma are spraying. The effect of ceramic coatings has also been investigated. The metallic coatings examined have been principally those of silicon, chromium, aluminum, zirconium and beryllium.⁽⁴⁸⁾ .

1-4 Aim of the work

A number of magnesium complexes are to be prepared which have suitable requirements of oil solubility and metal content as fuel additives to overcome the high temperature corrosion problem (vanadium attack problem). For this purpose a number of magnesium compounds are to be prepared with varying degrees of solubility, metal content and types of formulations as follows:

- 1- Preparation of a number of magnesium carboxylates using salts of mono- and di- carboxylic acids including derivatives of open chain, alicyclic and aromatic moieties.
- 2- Preparation of magnesium sulfonate.
- 3- Preparation of oil – water emulsion formulaties using two types of surfactant, one of them is magnesium derivative.
- 4- Study the solubility properties of all the prepared compounds and measuring the magnesium content using atomic absorption technique.
- 5- Study of the emulsion stability at different temperature and with respect to effect on the storage tanks.

Results and Discussion

The more efficient use of petroleum make the necessity for developing process which guarantee the optimum possible utilization of this raw material, especially with the shortage and increased costs of it.

The efficiency which can be achieved depends on the completeness of the combustion of the fuel with no side effect.

One way of achieving this aim is to add certain substance to the heating oil, which promote it's combustion and to minimize destructive side effects.

The description of the prior art in using various metals, presented in chapter one, known to improve combustion in boilers and combustion turbines show the magnesium to be the most widely used as a combustion catalyst in boilers with residual oil that often contains fuel contaminants, such as vanadium.

Due to incomplete description of the magnesium additives with respect to it's composition (the structure and the percent of the active magnesium), and also the relationship between the type of additive and the type of combustion engine, we found that it is necessary to prepare a wide range of magnesium compounds which include oil soluble (organic complexes), and emulsions .

The aim is also to find a new formulation of higher magnesium content with higher possible oil solubility.

3.1 Magnesium carboxylate:

Eleven sodium salts of mono and di- carboxylic acid including derivatives of open chain, alicyclic, and aromatic have been prepared by reaction of sodium hydroxide with the acid, except arachidic acid for which the sodium salt was not soluble, therefore it's potassium salt was prepared , on the other hand sodium oleate and sodium stearate were used as supplied.

The magnesium derivatives (or complexes)of all those salts were obtained by their reactions with magnesium chloride in aqueous medium Table (3-1) shows the melting points of all the prepared magnesium complexes and their respective carboxylic acid.

It can be shown that all the magnesium complexes have higher melting points than their respective acids, this was expected since the metal salts are known to have higher melting points especially when the size / charge ratio decreases, which is case with the studied metal ion (Mg^{+2}). Increasing the ionic charges will certainly increase the lattice energy of a crystal. For compounds which are predominantly ionic charges will result in increased melting points, and according to Fagan's rules, increasing charge results in increasing covalency, especially for small cation and large anions. Covalency does not necessarily favor either high or low melting points. For species which are strongly covalently bonded in the solid, but have weaker or fewer covalent bonds in the gas phase, melting and boiling points can be extremely high. It was found that low melting point salts have higher oil solubility⁽⁵⁷⁾ .

Table (3-1)also show the yield percent for the magnesium complexes, which are generally more than 87% excepted that of arachidate complex having 51% yield, this may be due to it's solubility difficulties

Table (3-1): the melting points of the magnesium complexes and their respective carboxylic acid and the yield percent.

Magnesium complex	Chemical structure	M.P.°C of related acid	M.P. °C	Yield %
Magnesium laurate	$(\text{CH}_3(\text{CH}_2)_{10}\text{COO})_2\text{Mg}$	42-44	140-142	96.78
Magnesium arachidate	$(\text{CH}_3(\text{CH}_2)_{18}\text{COO})_2\text{Mg}$	74-76	162-164	51.72
Magnesium palmitate	$(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2\text{Mg}$	62-64	≥ 300	94.83
Magnesium oleate	$(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_2\text{Mg}$	5-7	54-56	97.56
Magnesium stearate	$(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Mg}$	67-69	134-136	95.33
Magnesium Cyclohexane carboxylate	$(\text{C}_6\text{H}_{11}\text{COO})_2\text{Mg}$	29-31	58-60	97.4
Magnesium benzoate	$(\text{C}_7\text{H}_5\text{O}_2)_2\text{Mg}$	121-123	≥ 330	90.2
Magnesium cinnamate	$(\text{C}_6\text{H}_5\text{CH}=\text{CHCOO})_2\text{Mg}$	132-134	146-148	93.32
Magnesium adipate	$(\text{OOC}(\text{CH}_2)_4\text{COO})\text{Mg}$	151-153	>300	87.65
Magnesium phthalate	$(\text{C}_6\text{H}_4(\text{COO})_2)_2\text{Mg}$	212-214	296-298	96.71
Magnesium terphthalat	$(\text{C}_8\text{H}_4\text{O}_2)_2\text{Mg}$	≥ 300	328-330	89.49

The selected acid were chosen to get more than one variation, i.e. structural varieties and molecular weight varieties, in order to obtain magnesium complexes with higher possible metal content and in the same time higher oil solubility.

The oil is a pure hydrocarbon so it is non-polar. The non-polar hydrocarbon tail of the magnesium carboxylate dissolves into the oil. That leaves the polar carboxylate ion of the molecules are sticking out of the oil droplets, the surface of each oil droplet is negatively charged. As a result, the oil molecules dissolve the magnesium carboxylate when the polarity of magnesium carboxylate became less⁽⁵⁸⁾.

The bonding and structure of carboxylate salts is somewhat involved. They contain atoms bonded to one another by a variety of bond types: nonpolar covalent bonds, polar covalent bonds and ionic bonds. The distinguishing structural feature is the carboxylate moiety. In their pure form carboxylate salts are ionic compounds⁽⁵⁹⁾.

Two factors determine the solubility of carboxylate salts in oil. One is the nature of the carboxylate ion, i.e. its length, shape, amount of branching and so on. The larger and less polar this group is, the more soluble it is in oil. Solubility of five-carbon-atom in water is not appropriate for carboxylate ions. The reason is that the carboxylate functional group is not merely polar, it is ionic. This allows for stronger ion-dipole bonds to be formed with the water molecules and pull longer carbon chains into solutions. Soaps, for example, generally have from twelve to eighteen carbon atoms in the carbon chain.

The other factor is the positive ion. Ammonium, potassium and sodium salts are generally soluble in water. Magnesium and calcium salts are generally less soluble. Many others are generally insoluble. For example, a soap containing sodium ion will dissolve in water.

However, if the water contains magnesium, calcium or iron, these ions will take the place of the sodium ions, combine with the carboxylate ion to make an insoluble compound and precipitate out of solution to form what is commonly called metal carboxylates⁽⁶⁰⁾.

Table (3-2) and fig (3-1) show that magnesium oleate to be higher solubility among the magnesium carboxylate, the reason of it's higher solubility may be related to the length of the hydrocarbon chain of the oleate molecules and the presence of unsaturated double bond which affect it's solubility. On comparison of the solubility of two(C₁₈) acids (stearate, and oleate), magnesium oleate have higher solubility than it's stearate analogue, this is due to the presence of a double bond in the oleate only. The solubility of the studied magnesium carboxylate was generally higher in gas-oil than in the other solvent, as seen in fig (3-2).

The magnesium salt of an organic acid with sufficient lipophilic character to achieve oil solubility contains less than 6% magnesium by weight. It was thought that the reason is that a molecular weight of about 200 is required for the organic acid to have oil solubility and the elemental weight of magnesium is 24. Magnesium is a divalent element and two acid molecules are required for each atom of magnesium⁽⁴²⁾.

Table (3-3) show that magnesium adipate has higher magnesium content (14.28 %) and magnesium arachidate has lower metal content (3.715%). Fig (3-4) show that as the molecular weight increases the metal content decreases. An attempt was made to get a complex of higher possible solubility with simultaneous higher possible metal content. Complexes with high metal content but poor solubility are of no use. It's was found that magnesium oleate and magnesium stearate were of higher solubility and higher possible metal content, as seen in tables (3-2, 3-3) and fig (3-1,3-2,3-3).

It was studied that (3 magnesium : 1 vanadium) ratio is needed to treated the hot corrosion⁽⁶¹⁾, in this work the highest soluble complex was of (3.52 %) magnesium content, which is comparable with those additives described in the US patents No. 5145488⁽⁶¹⁾, 4229309⁽⁶²⁾, 4179383⁽⁶³⁾, 4293429⁽⁶⁴⁾, 4298482⁽⁶⁵⁾, and 4226739⁽⁶⁶⁾.

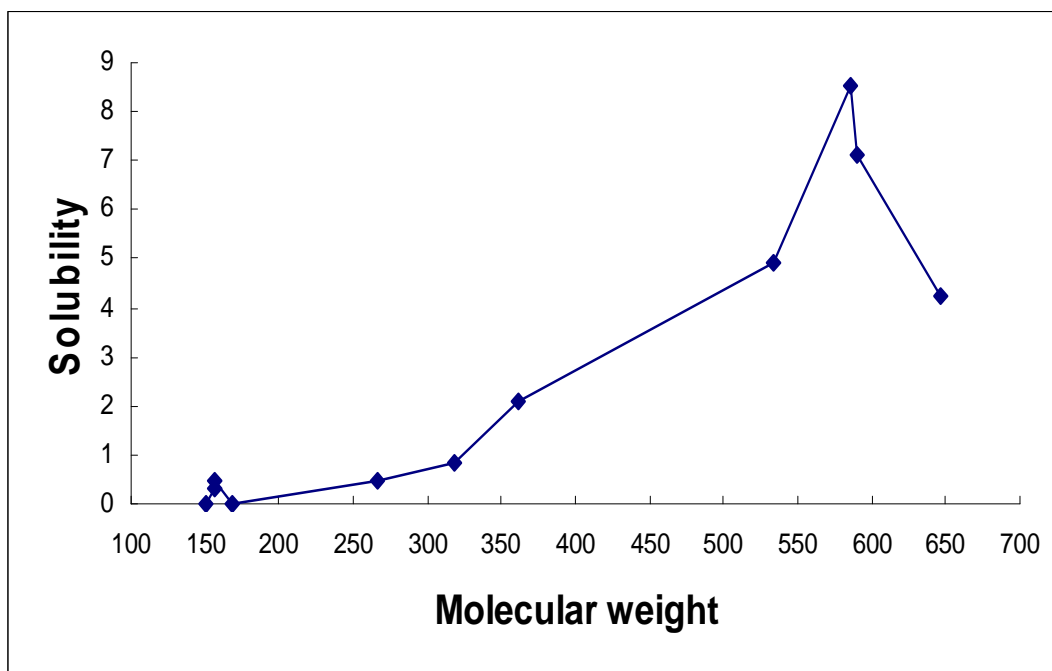


Figure (3-1) solubility of prepared magnesium carboxylate with it's molecular weight

Table (3-2) solubility of magnesium carboxylate in different solvents

Mg com. \ solvent	Xylene	Toluene	Gas oil
Magnesium laurate	1.95	1.86	2.11
Magnesium arachidate	3.24	3.44	4.25
Magnesium palmitate	4.86	4.82	4.92
<i>Magnesium oleate</i>	8.41	8.46	8.51
<i>Magnesium stearate</i>	7.08	7.02	7.13
MagnesiumCyclohexane carboxylate	Insoluble	Insoluble	Insoluble
Magnesium benzoate	0.46	0.49	0.47
Magnesium cinnamate	0.88	0.85	0.85
Magnesium adipate	Insoluble	Insoluble	Insoluble
Magnesium phthalate	0.52	0.47	0.48
Magnesium terphthalate	0.29	0.31	0.30

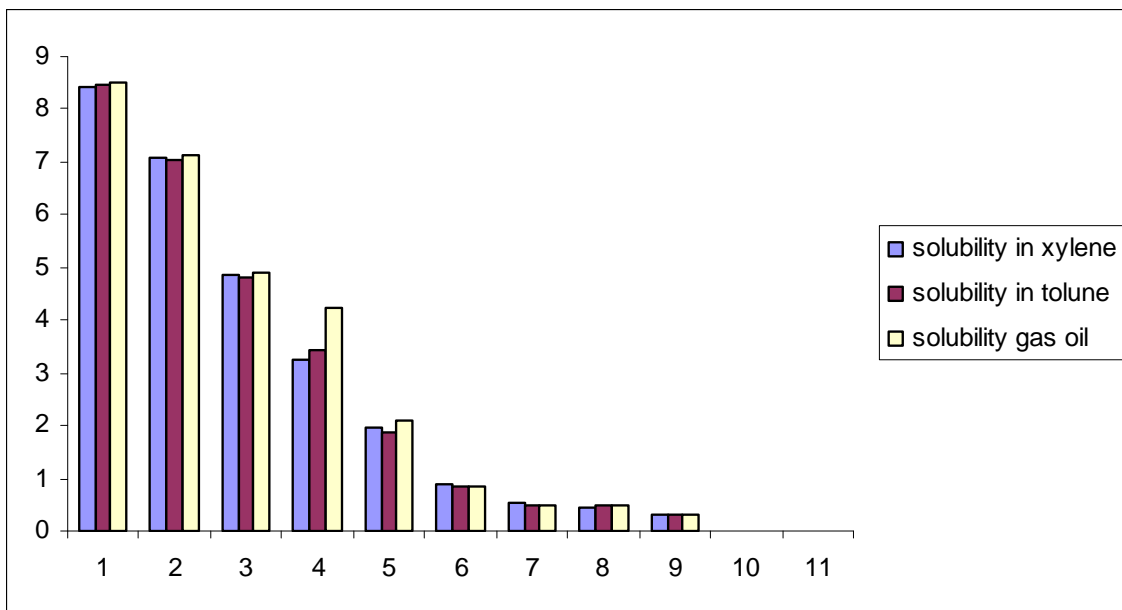


Figure (3-2) solubility of prepared complexes in deferent solvents

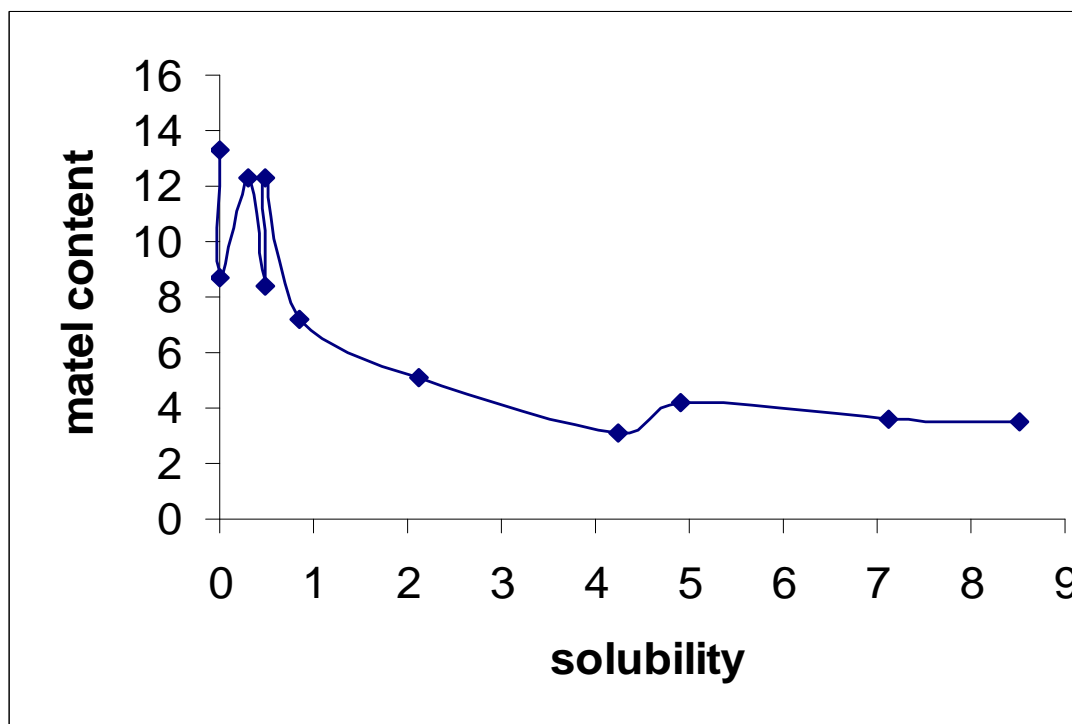


Figure (3-3) solubility of prepared complexes with it's metal content

Table (3-3) magnesium content of the prepared complexes

Compound	Chemical structure	Theoretical value	Practical value
Magnesium laurate	$(\text{CH}_3(\text{CH}_2)_{10}\text{COO})_2\text{Mg}$	5.68	5.06
Magnesium arachidate	$(\text{CH}_3(\text{CH}_2)_{18}\text{COO})_2\text{Mg}$	3.715	3.12
Magnesium palmitate	$(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2\text{Mg}$	4.494	4.17
<i>Magnesium oleate</i>	$(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_2\text{Mg}$	4.095	3.52
<i>Magnesium stearate</i>	$(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Mg}$	4.067	3.64
Magnesium phthalate	$(\text{C}_8\text{H}_4\text{O}_2)\text{Mg}$	12.765	12.28
Magnesium terphthalate	$(\text{C}_8\text{H}_4\text{O}_2)\text{Mg}$	12.765	12.33
Magnesium benzoate	$(\text{C}_7\text{H}_5\text{O}_2)_2\text{Mg}$	9.022	8.39
Magnesium Cyclohexane carboxylate	$(\text{C}_7\text{H}_{11}\text{O}_2)\text{Mg}$	9.561	8.75
Magnesium cinnamate	$(\text{C}_6\text{H}_5\text{CH}=\text{CHCOO})_2\text{Mg}$	7.54	7.23
Magnesium adipate	$(\text{OOC}(\text{CH}_2)_4\text{COO})\text{Mg}$	14.28	13.35

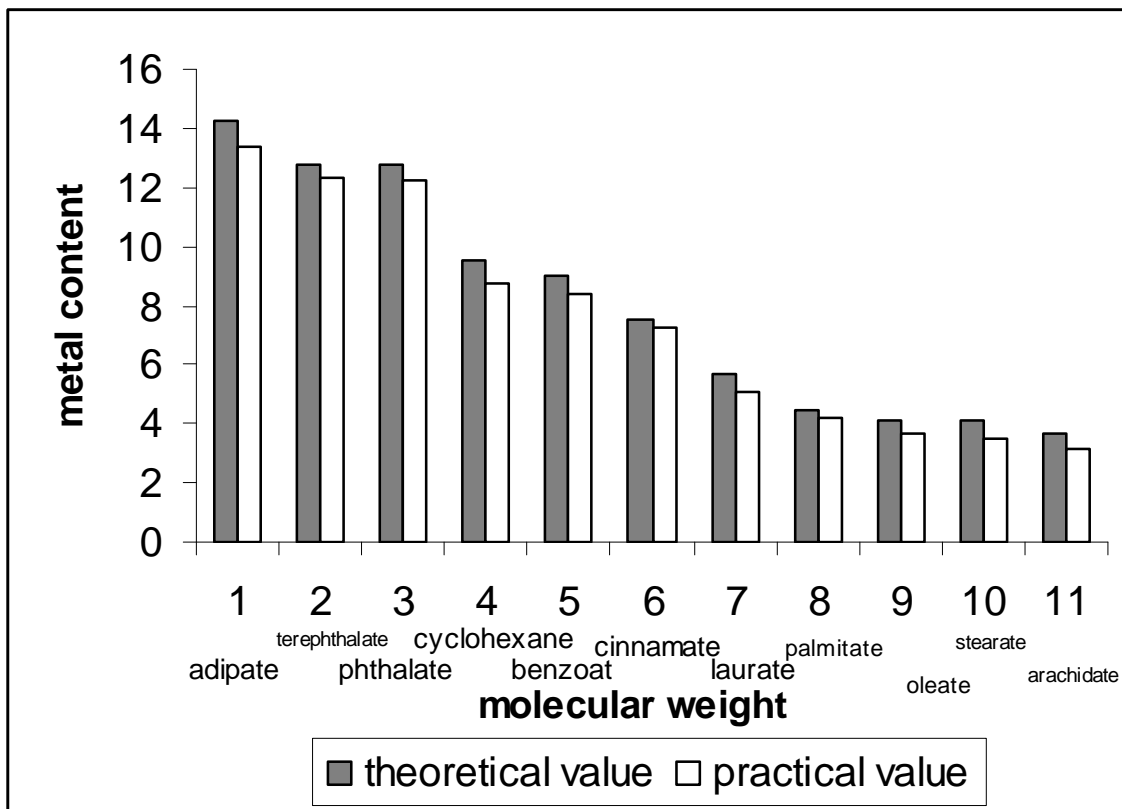


Figure (3-4) metal content of prepared complexes

3-2 Infrared spectra of the prepared complexes:

All the spectra of the prepared magnesium carboxylates were recorded in the solid state using KBr disk in the range (4000-400) cm^{-1} .

All the compounds contain an important diagnostic group; this is a carbonyl group (C=O). In general carbonyl stretching absorption frequency occurs around (1710) cm^{-1} depending on nature of groups linked to it⁽⁶⁷⁾. The compounds containing carbonyl group show basic behavior toward metal ions coordinating via the oxygen atoms, this coordination shifts the stretching frequency of carbonyl (C=O) group toward lower value in some complexes, the decrease value in frequency indicates a decrease in the stretching force constant of (C=O) group as a consequence of the coordination through other groups. The double bond character between carbon and oxygen is reduced⁽⁶⁸⁾.

The stretching frequency band of the (O-H) group appeared in the spectra of some carboxylic acids in the rang (3100-3500) cm^{-1} , this band found down field (at about 2990 cm^{-1}) due to strong hydrogen bonding⁽⁶⁹⁾.

When the carboxylic acid react with magnesium salt, magnesium carboxylate have been therefore a red shift in the (ν C=O) took place in all of the complexes, this because the bond order of the carbonyl group was decreases.

Figures (3-5 ----- 3-26) show the spectra of all the prepared complexes.

Table (3-4) summarize the most diagnostic IR absorption frequencies of the magnesium carboxylate.

These results indicate the coordination of magnesium ion with the selected carboxylate.

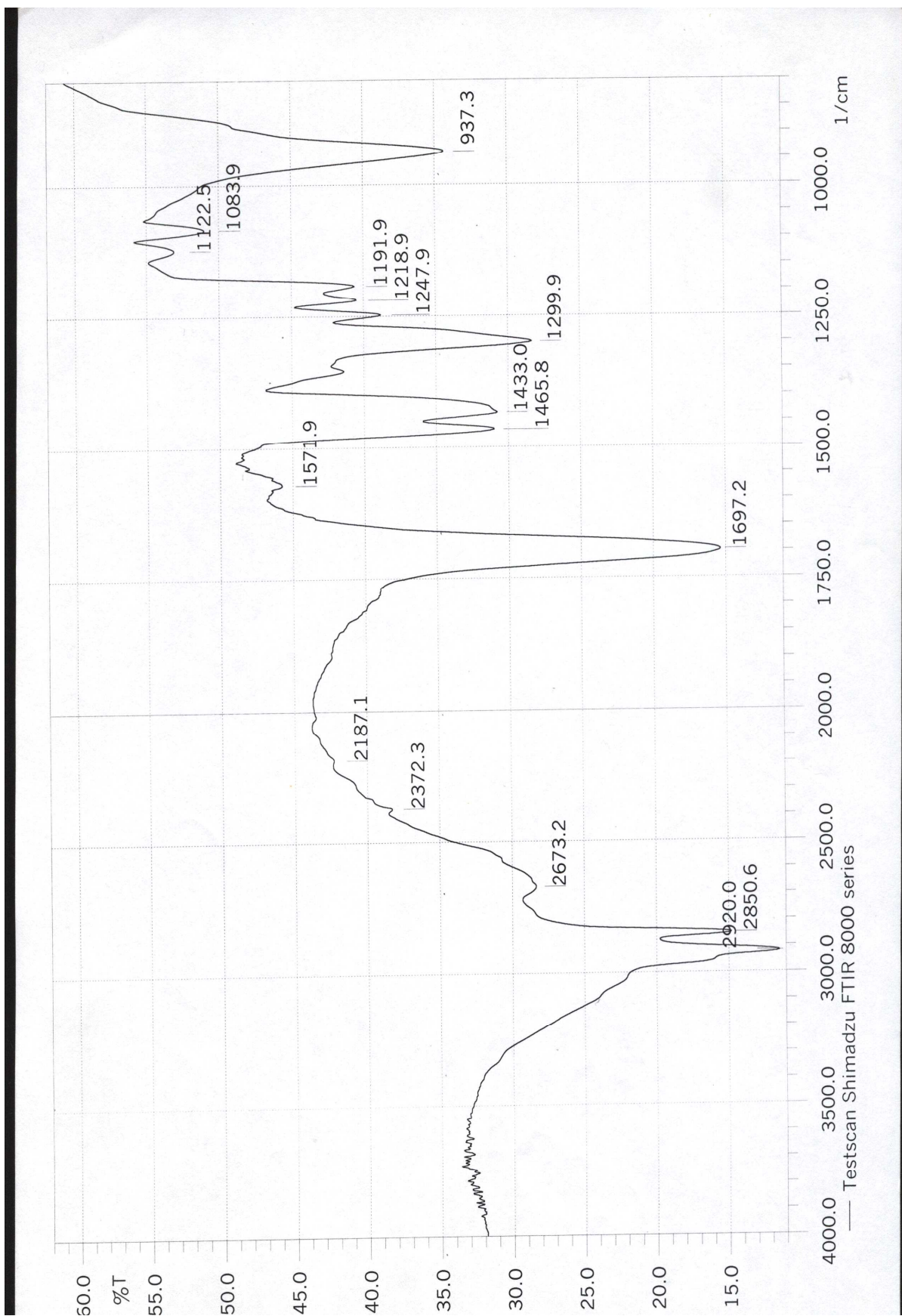


Figure (3-5) F.T.IR spectrum of lauric acid

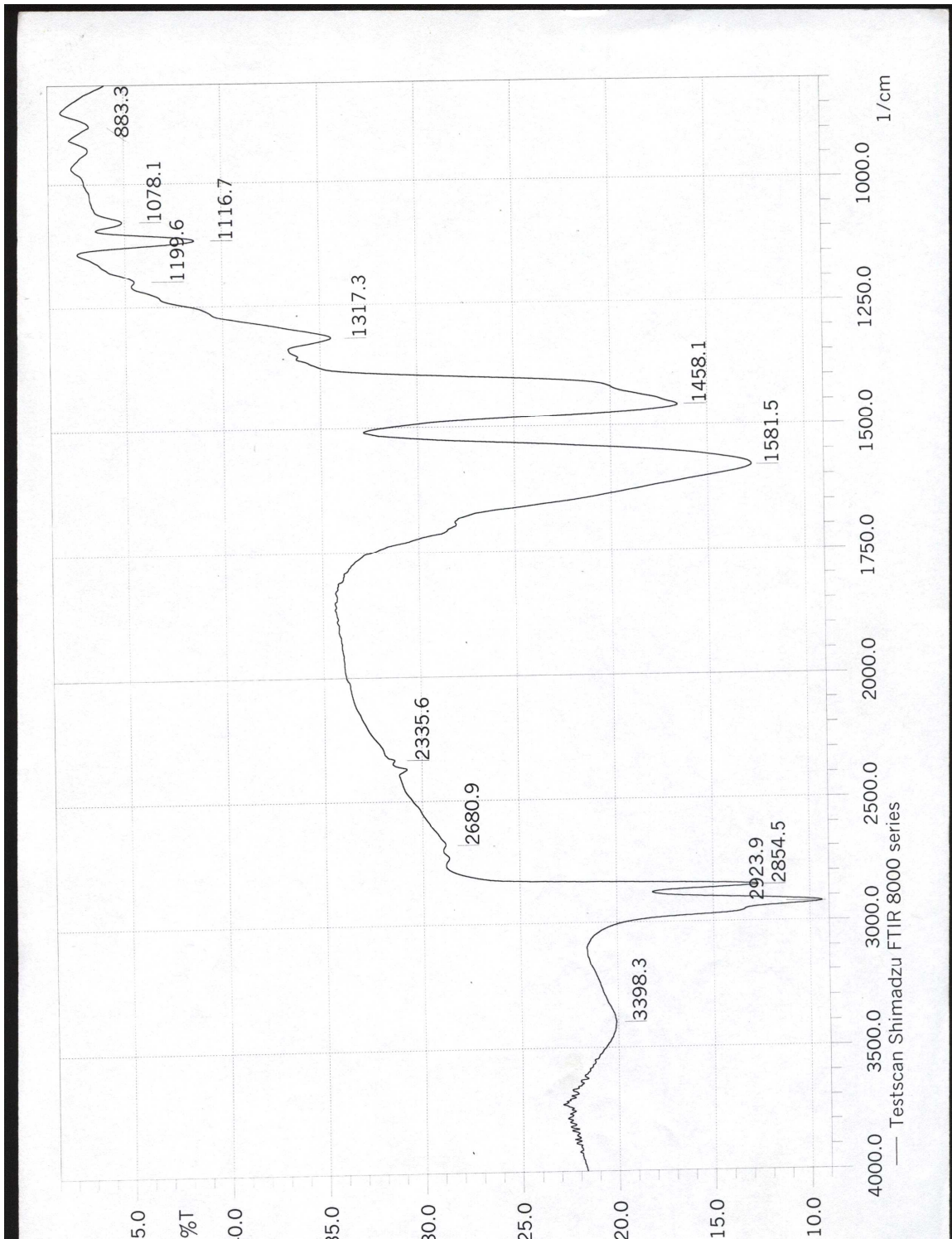


Figure (3-6) F.T.IR spectrum of Magnesium laurate

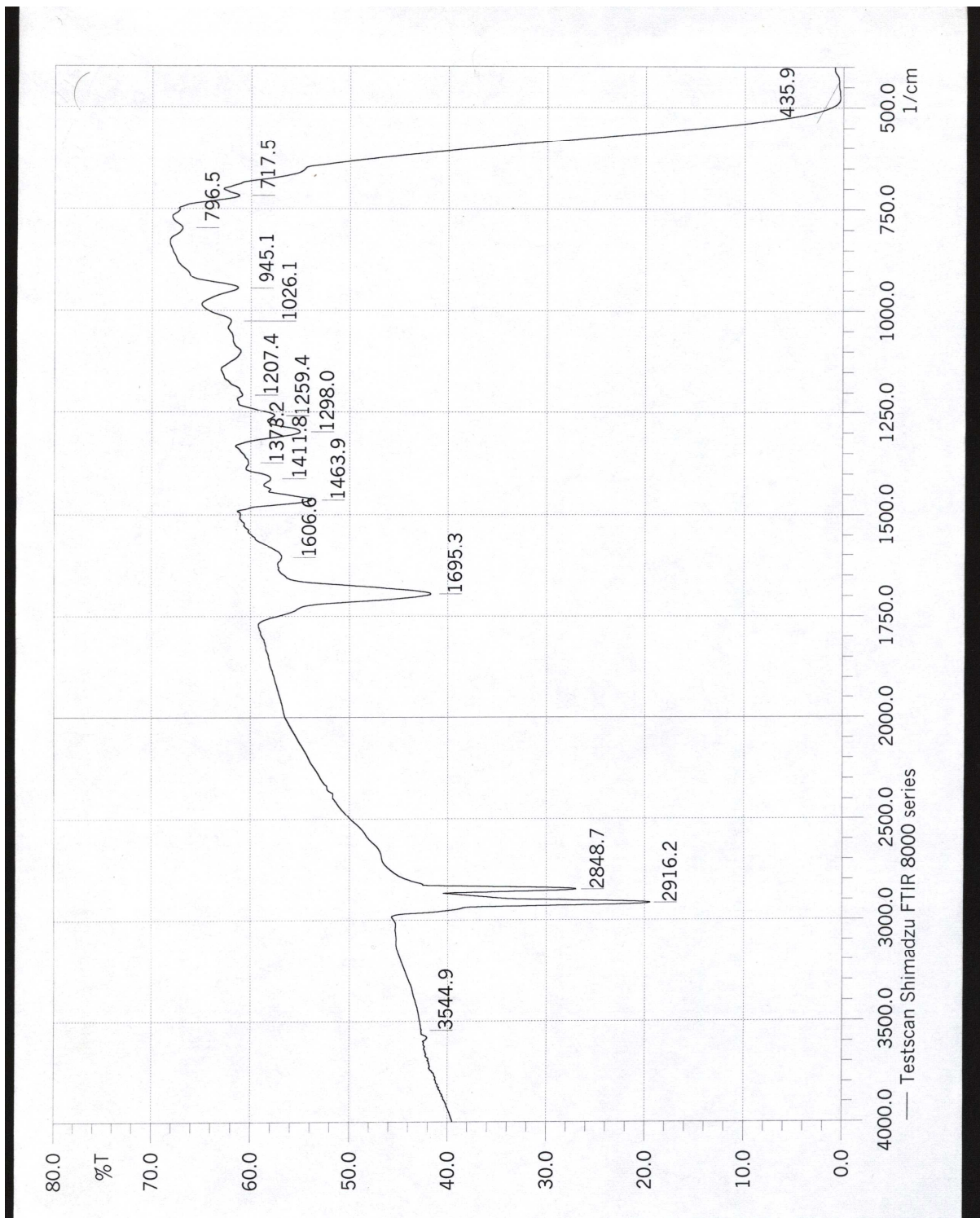


Figure (3-7) F.T.IR spectrum of arachidic acid

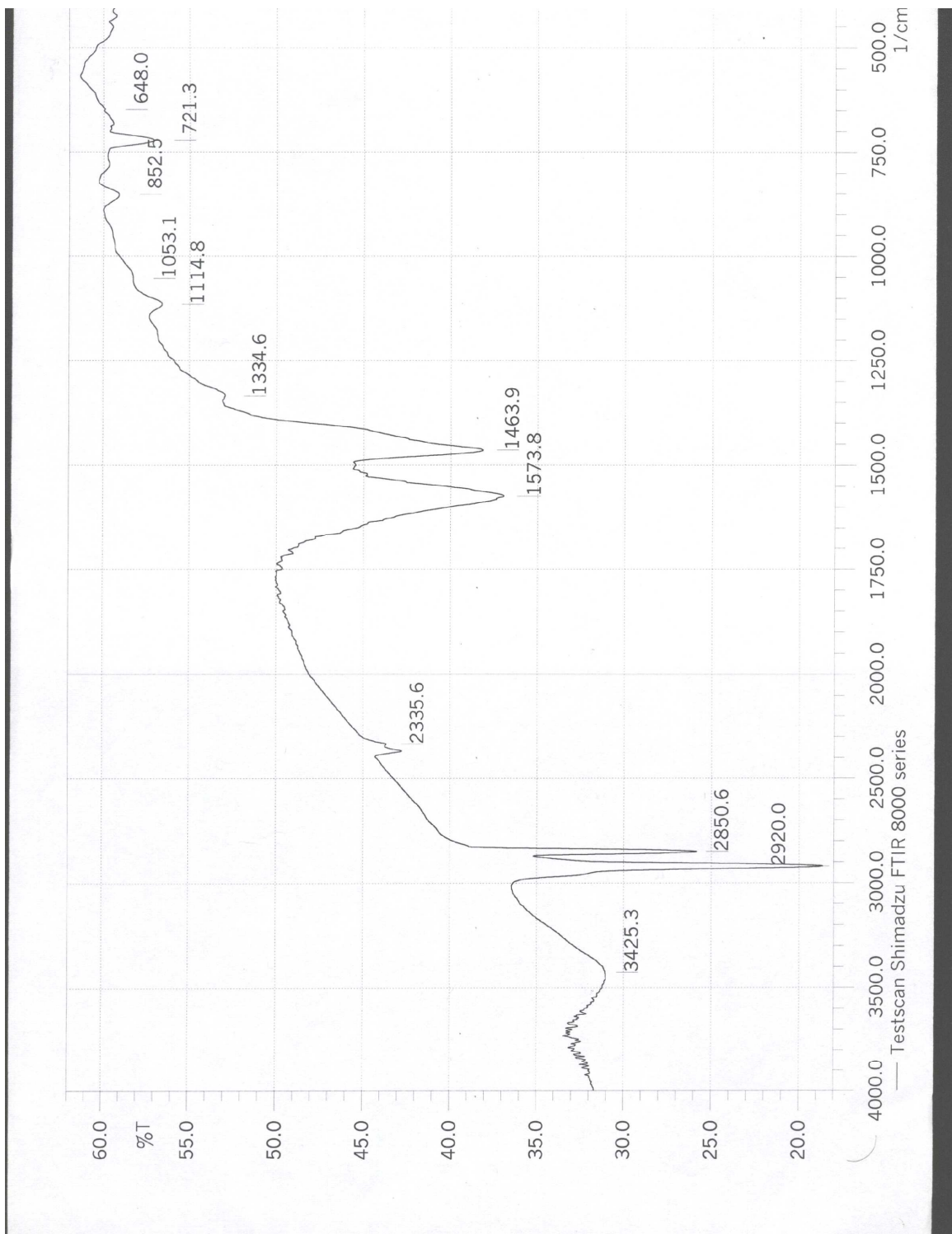


Figure (3-8) F.T.IR spectrum of Magnesium arachidate

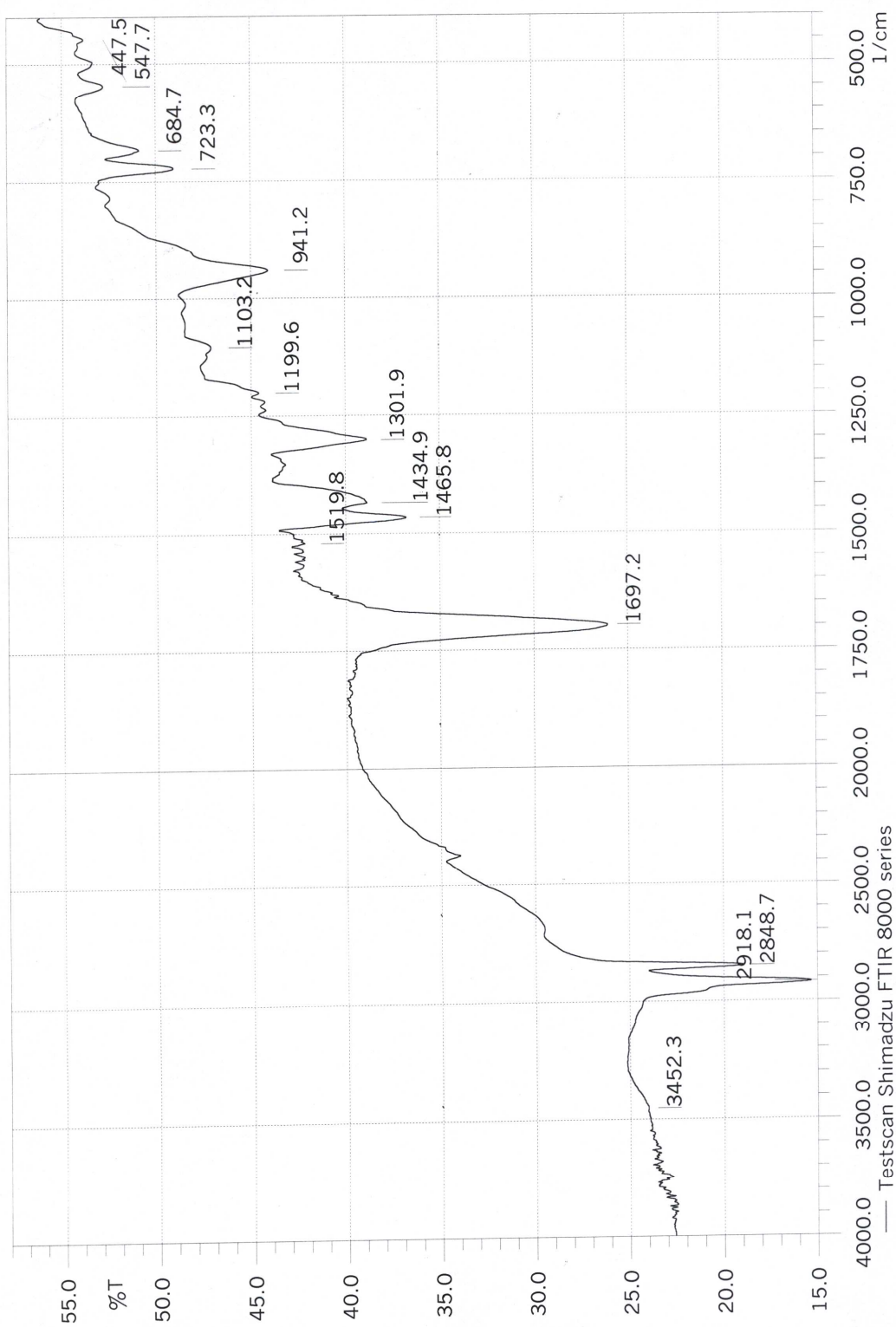


Figure (3-9) F.T.IR spectrum of Palmitic acid

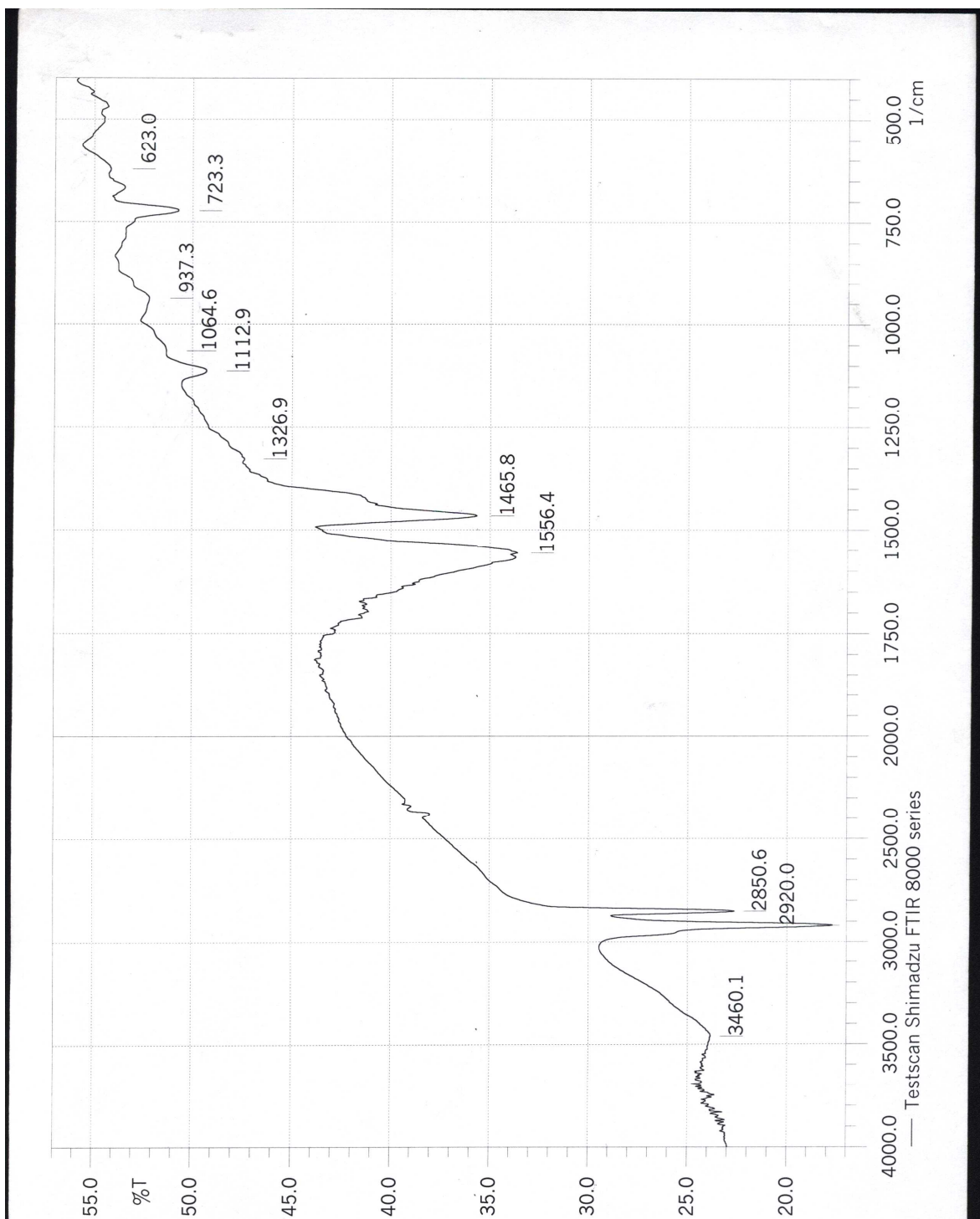


Figure (3-10) F.T.IR spectrum of magnesium palmitate

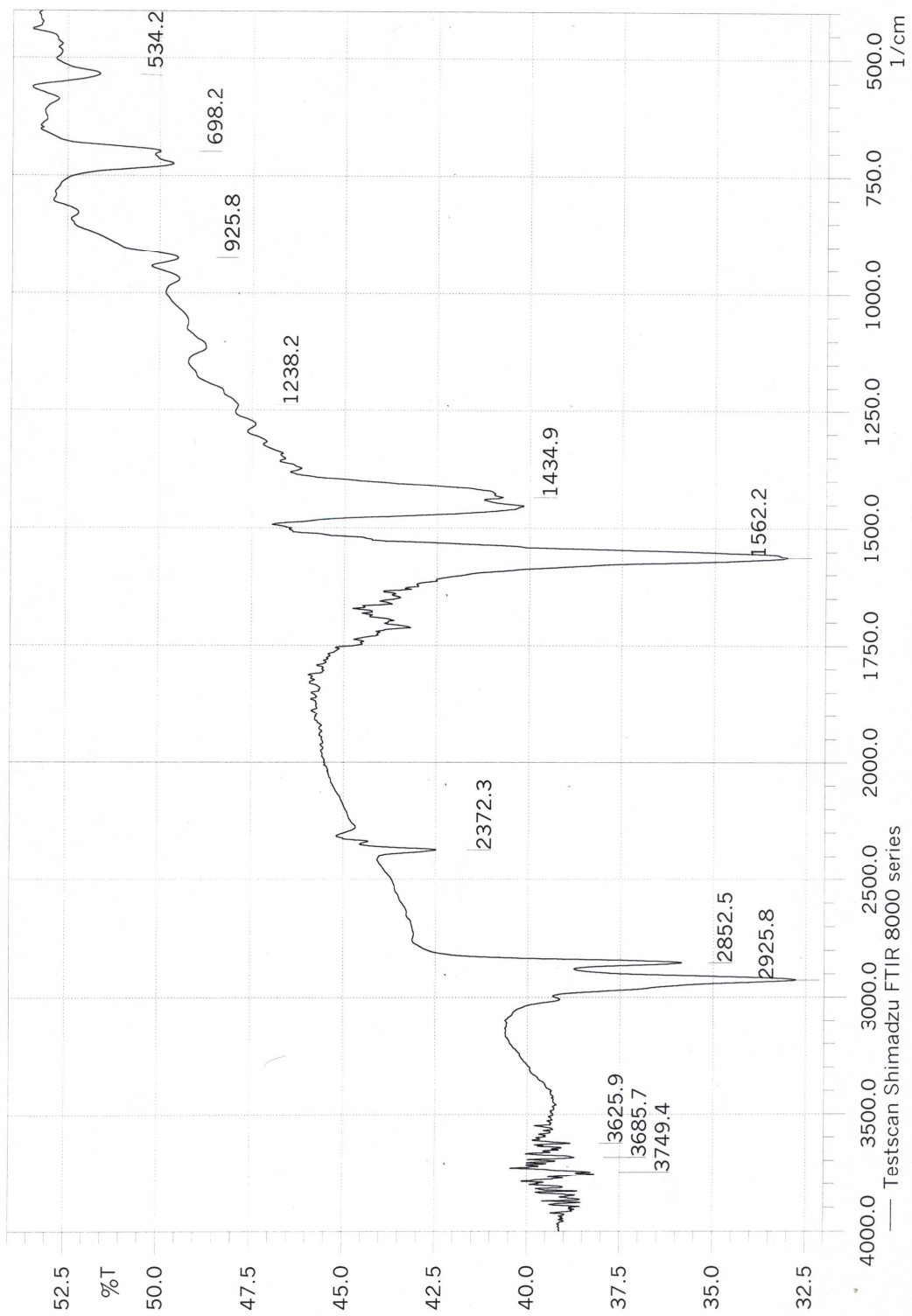


Figure (3-11) F.T.IR spectrum of sodium oleate

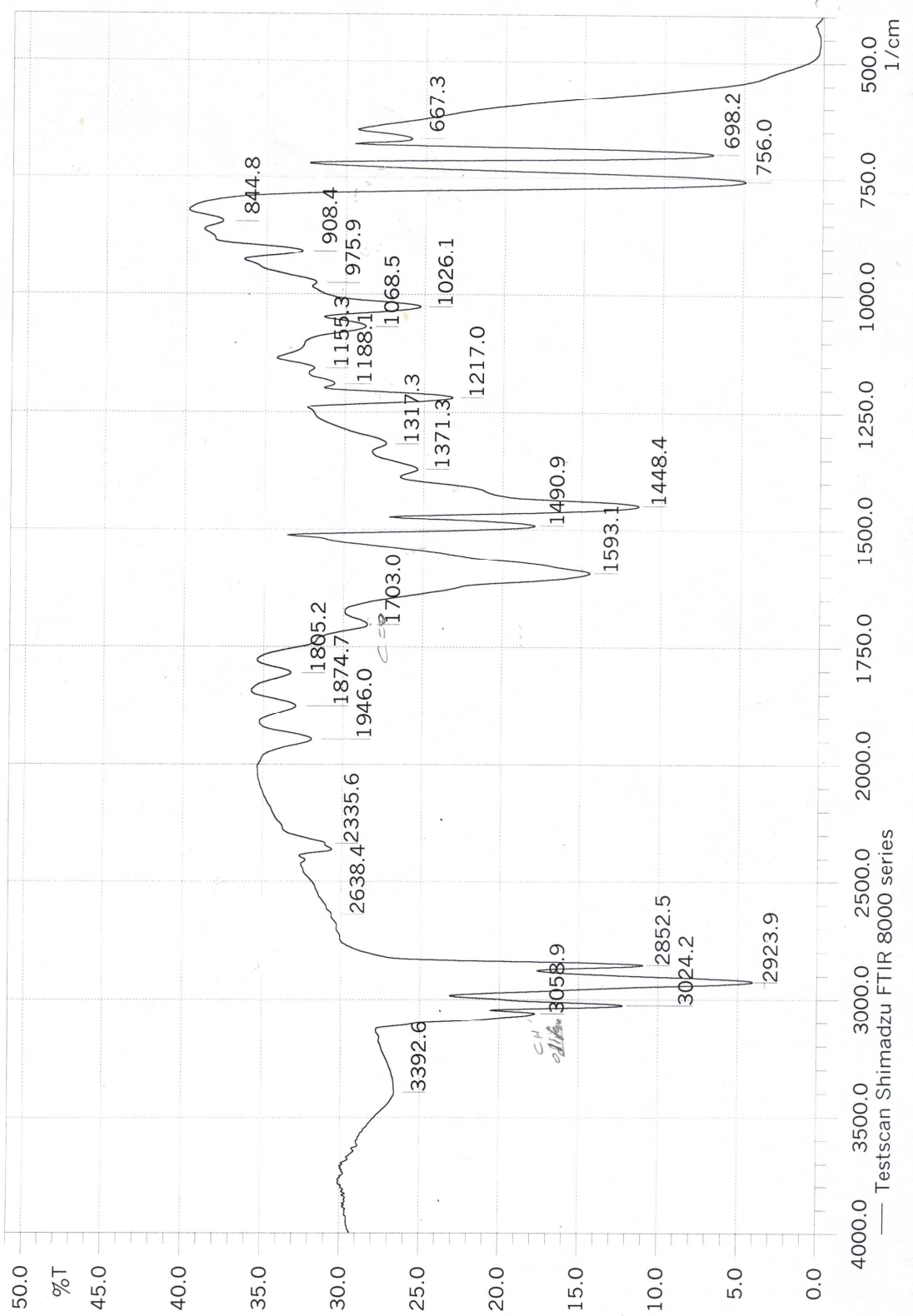


Figure (3-12) F.T.IR spectrum of magnesium oleate

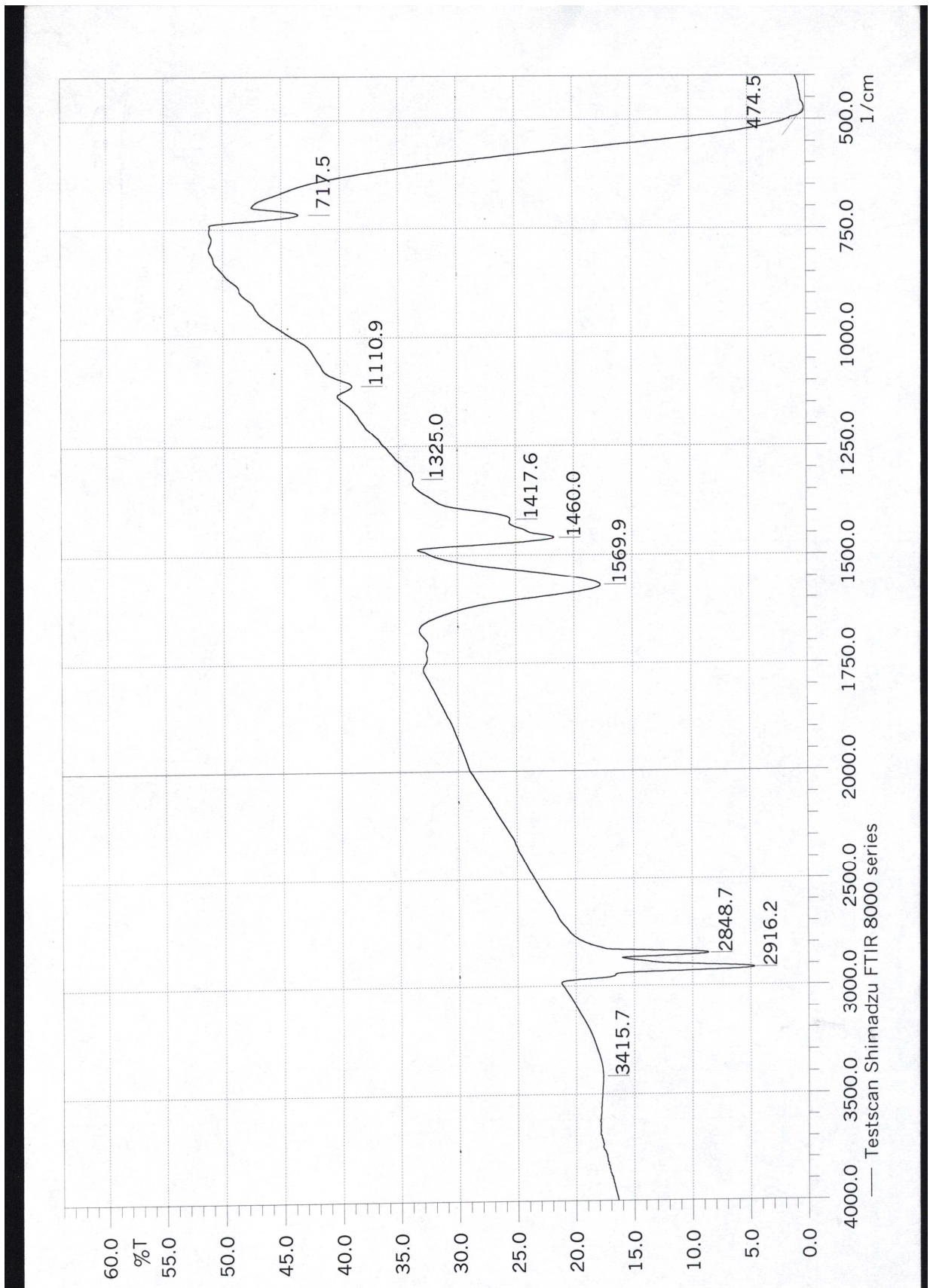


Figure (3-13) F.T.IR spectrum of sodium stearate

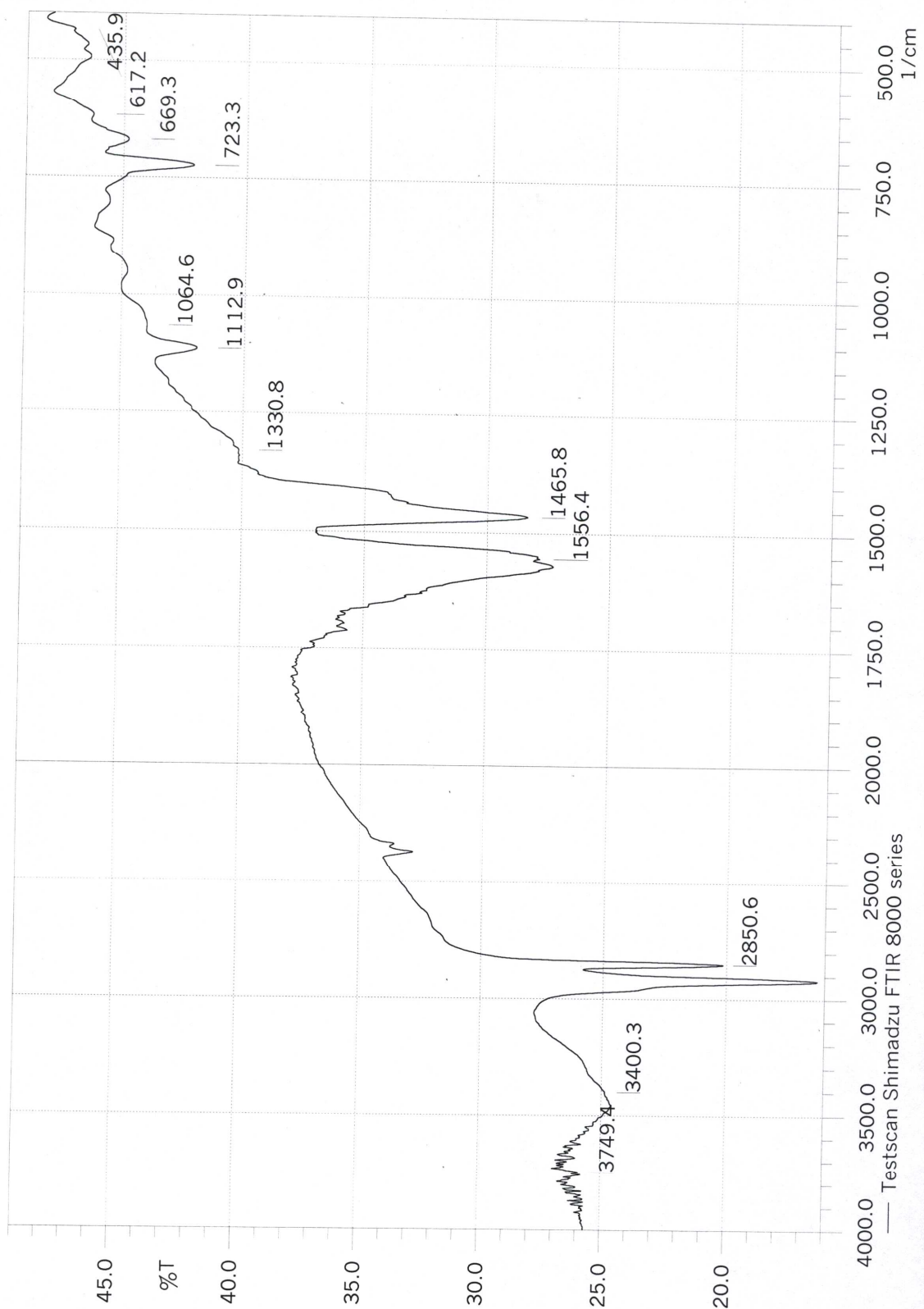


Figure (3-14) F.T.IR spectrum of magnesium stearate

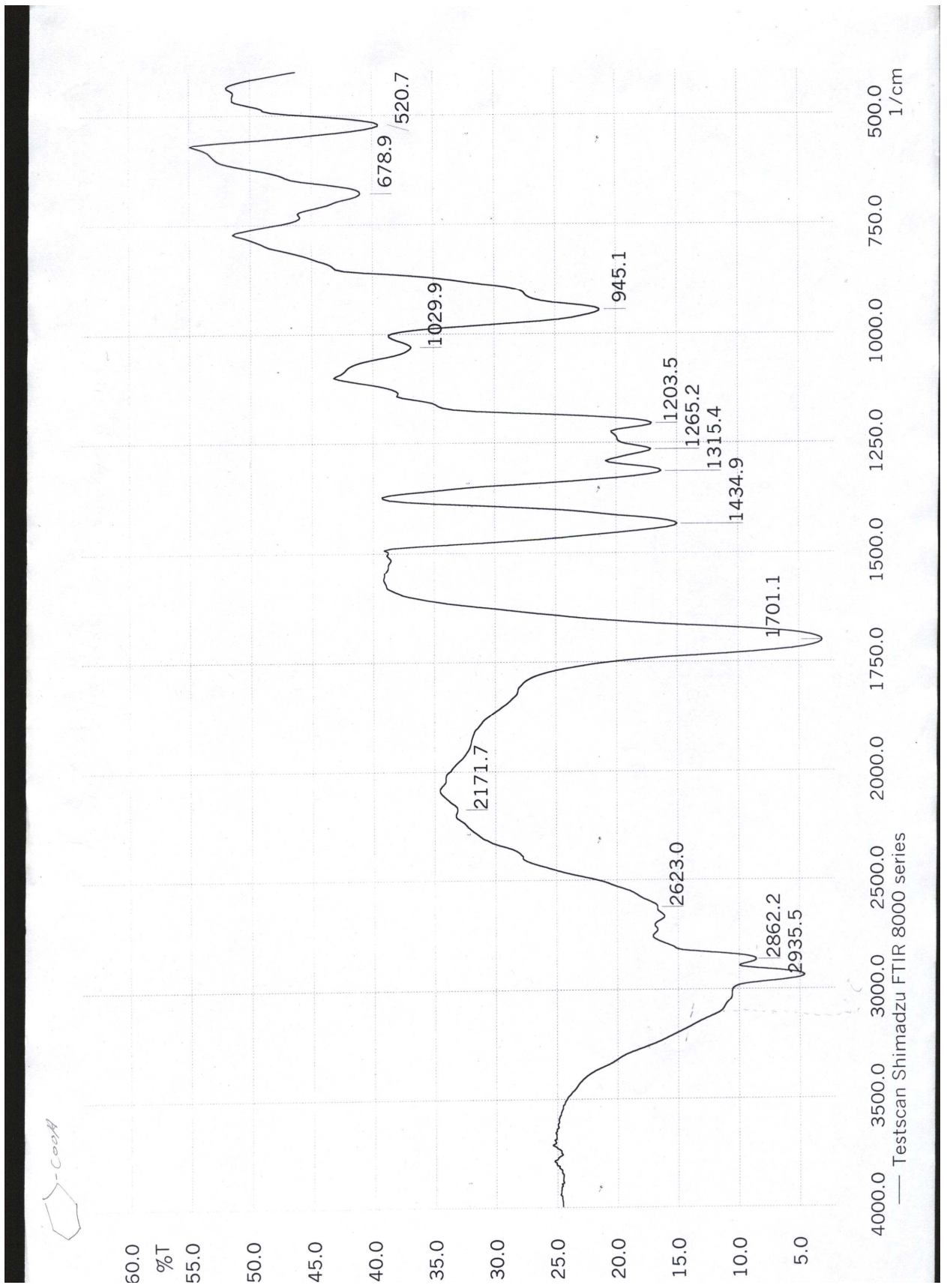


Figure (3-15) F.T.IR spectrum of cyclohexane carboxylic acid

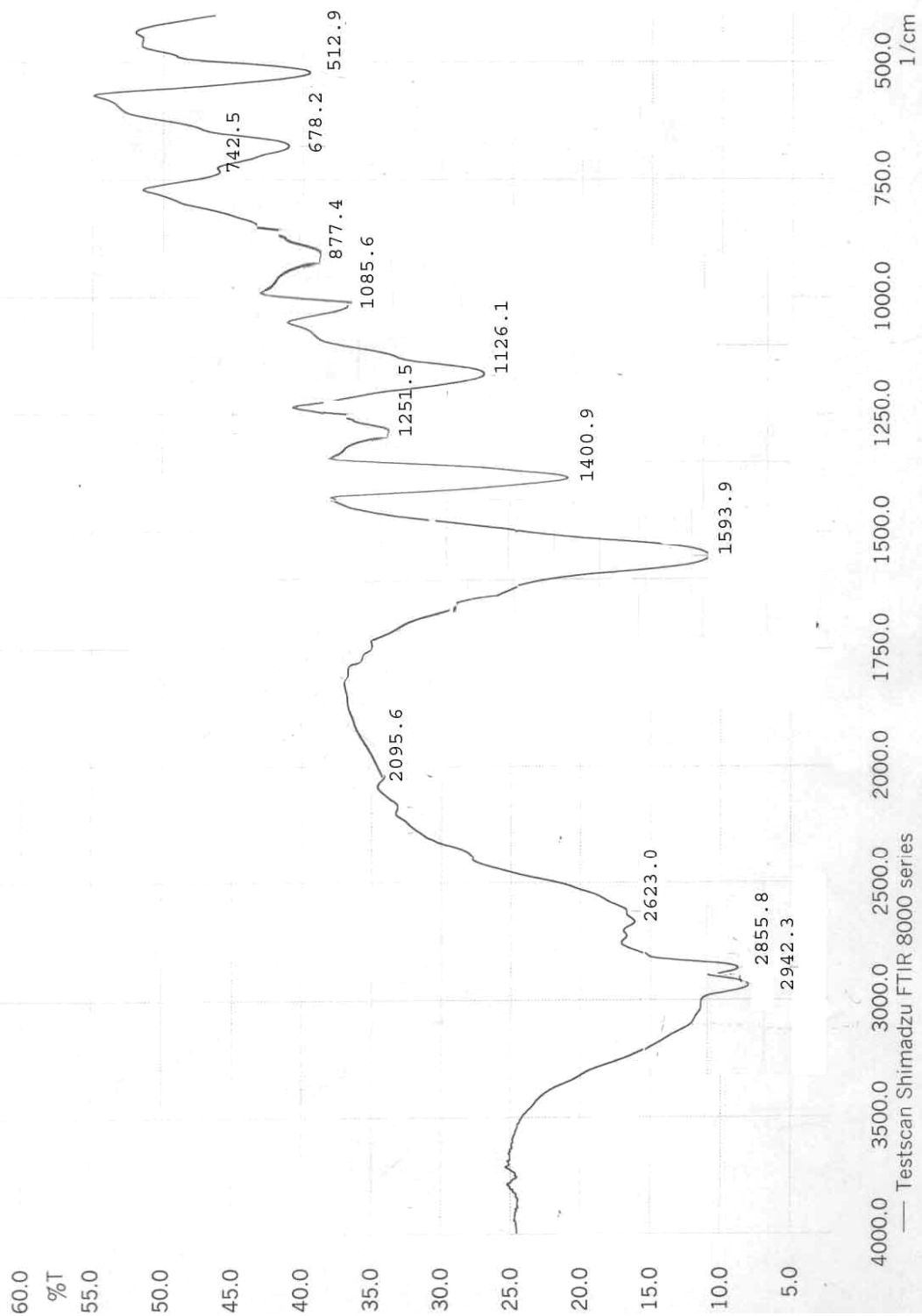


Figure (3-16) F.T.IR spectrum of magnesium cyclohexane carboxylic acid

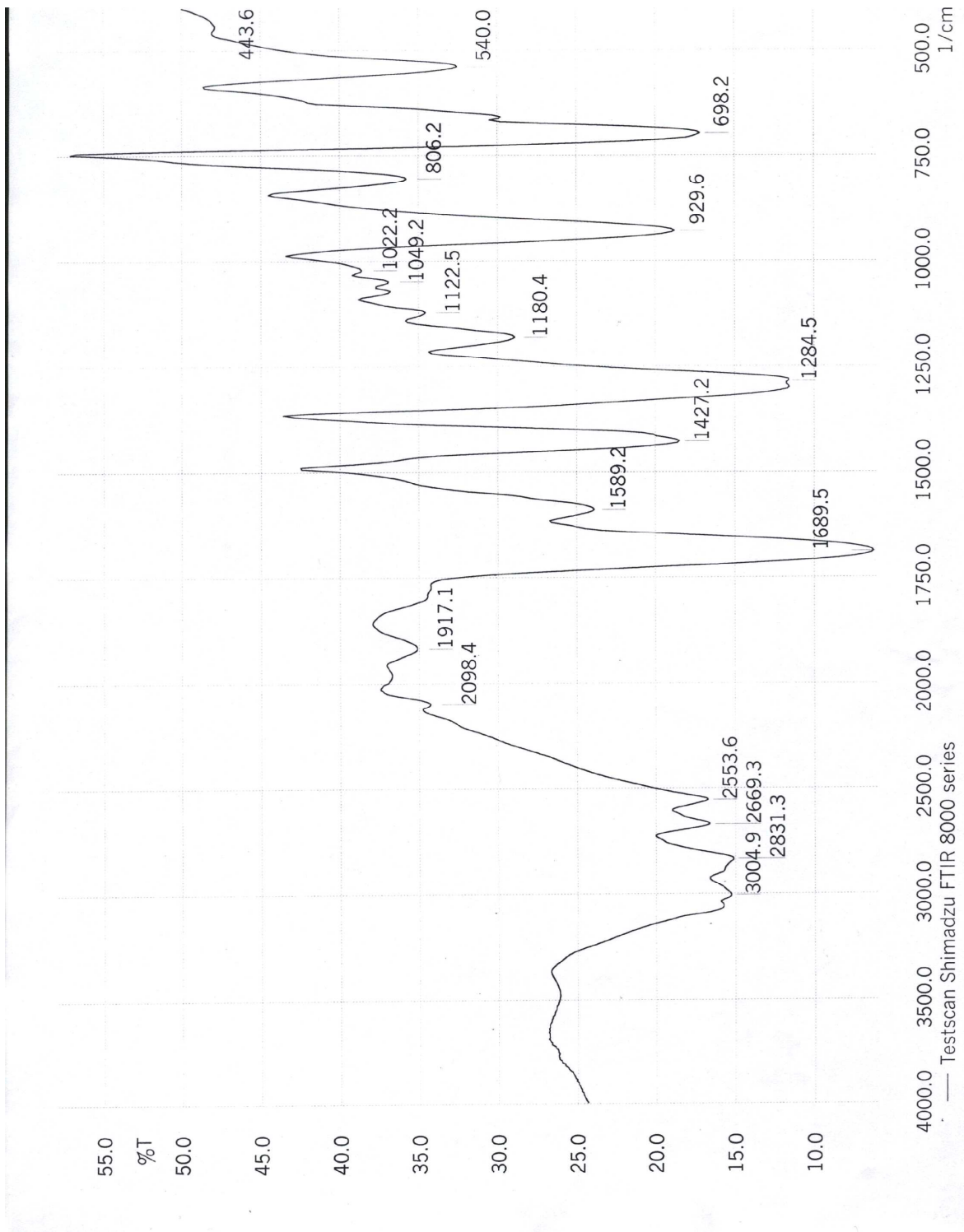


Figure (3-17) F.T.IR spectrum of benzoic acid

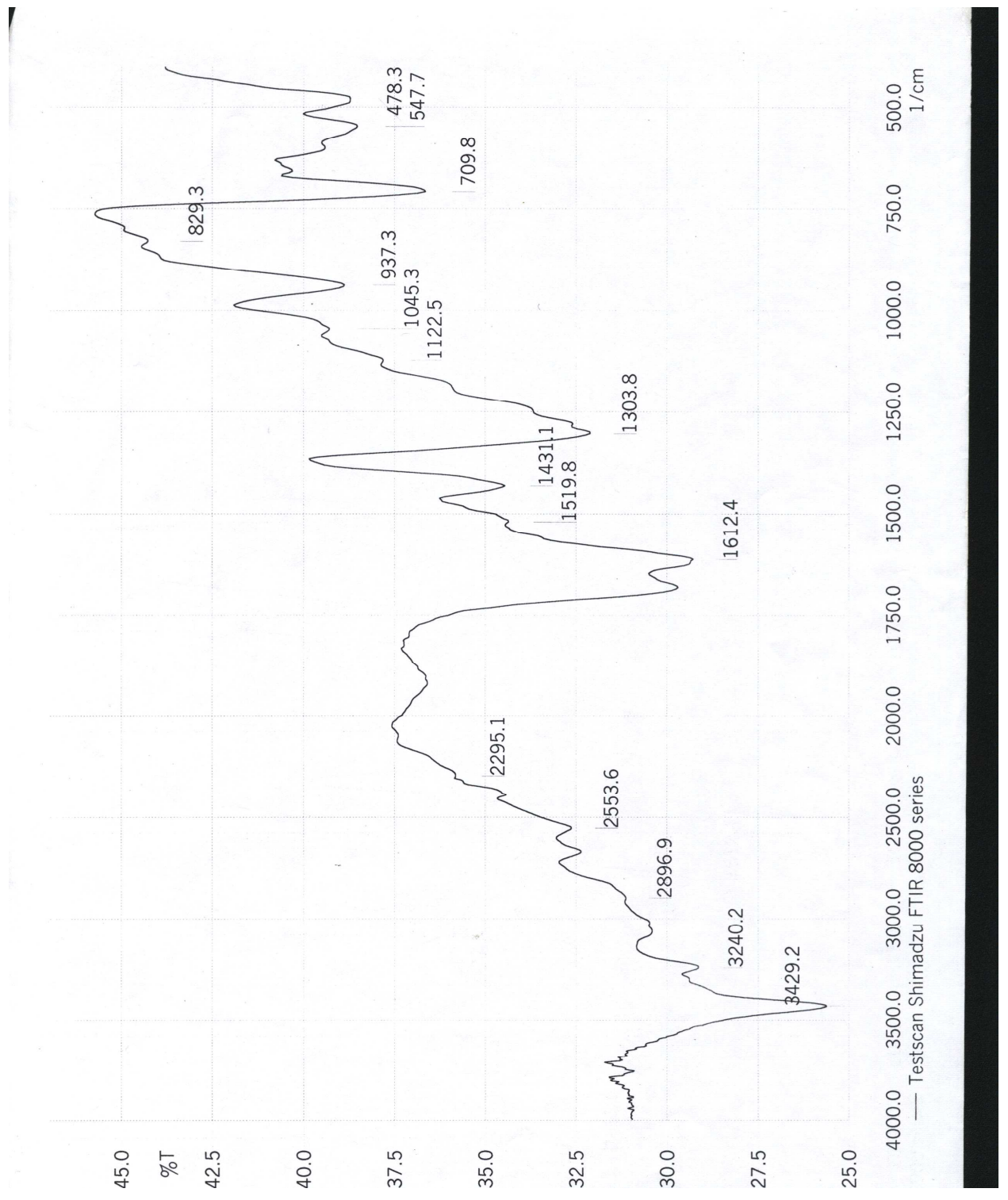


Figure (3-18) F.T.IR spectrum of magnesium benzoate

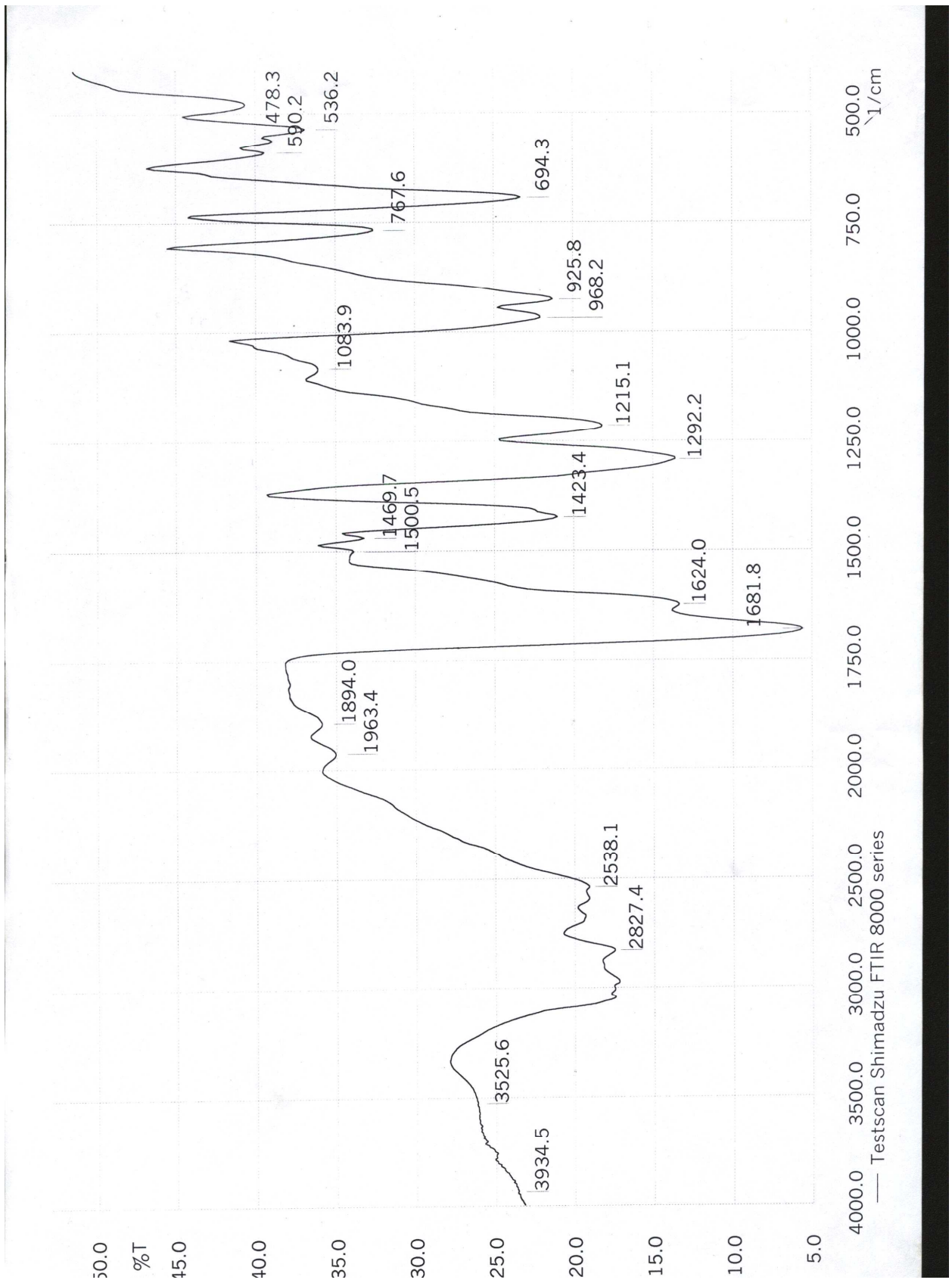


Figure (3-19) F.T.IR spectrum of cinnamic acid

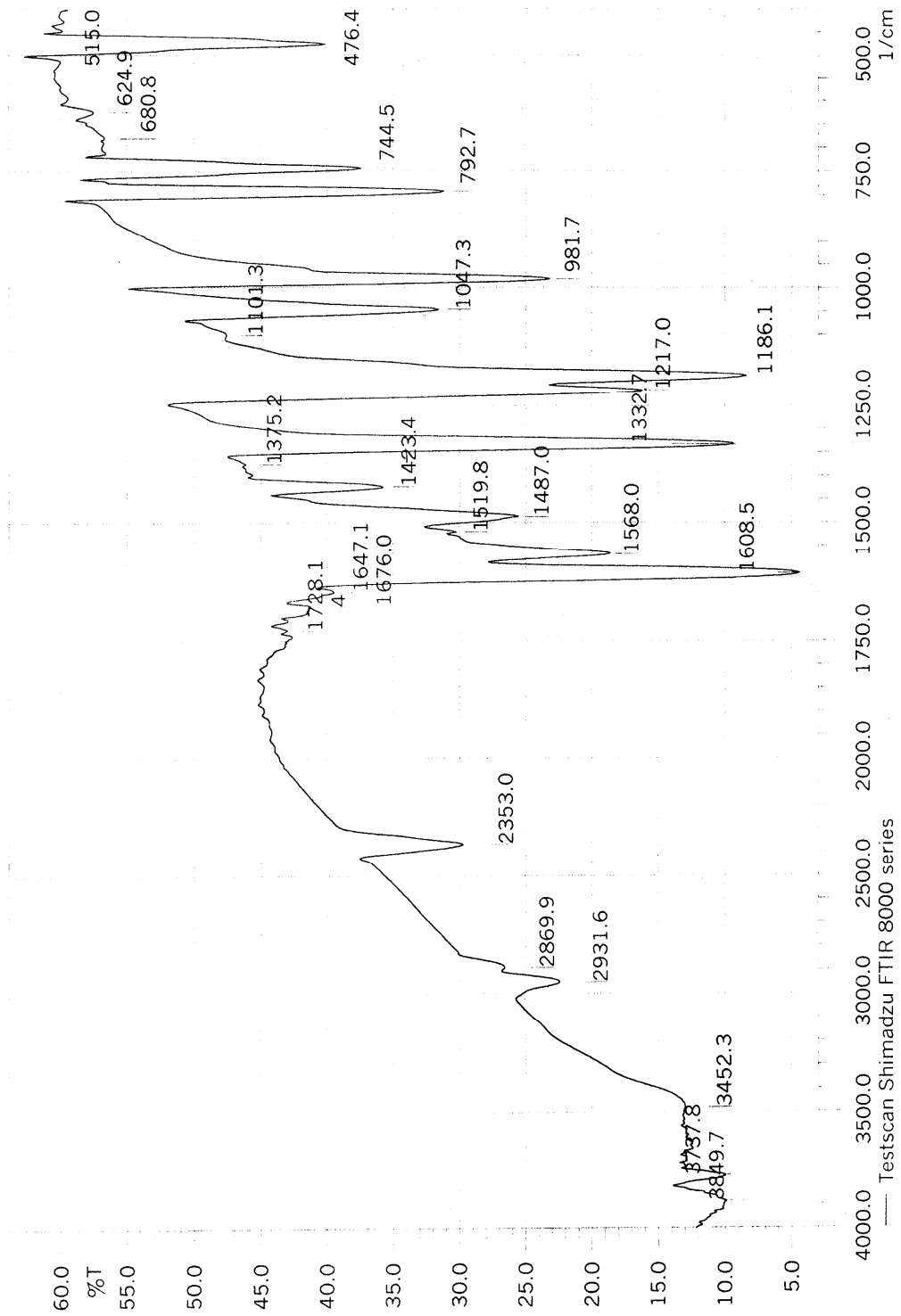
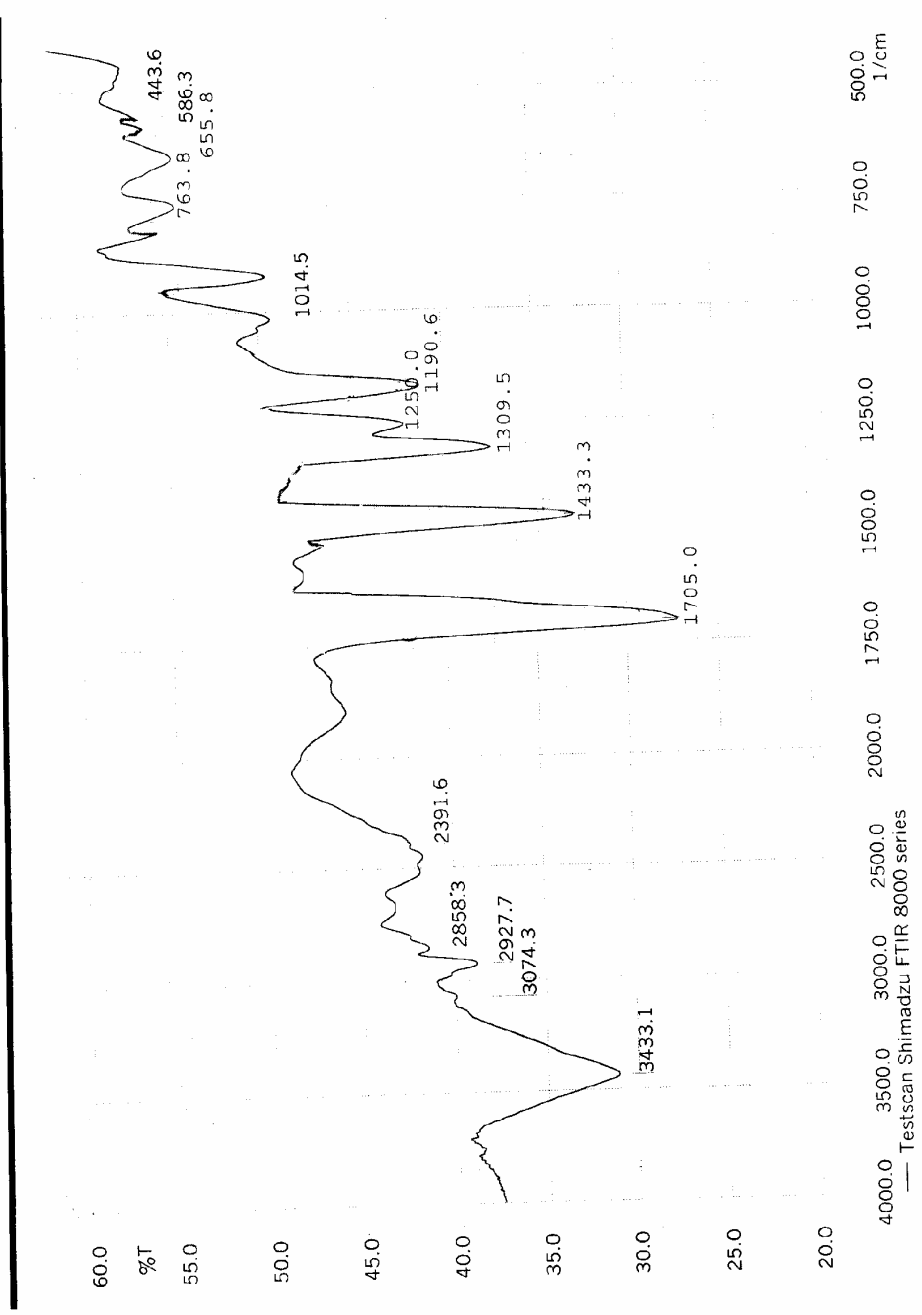


Figure (3-20) F.T.IR spectrum of magnesium cinnamate



(Figure 3-21) F.T.IR spectrum of adipic acid

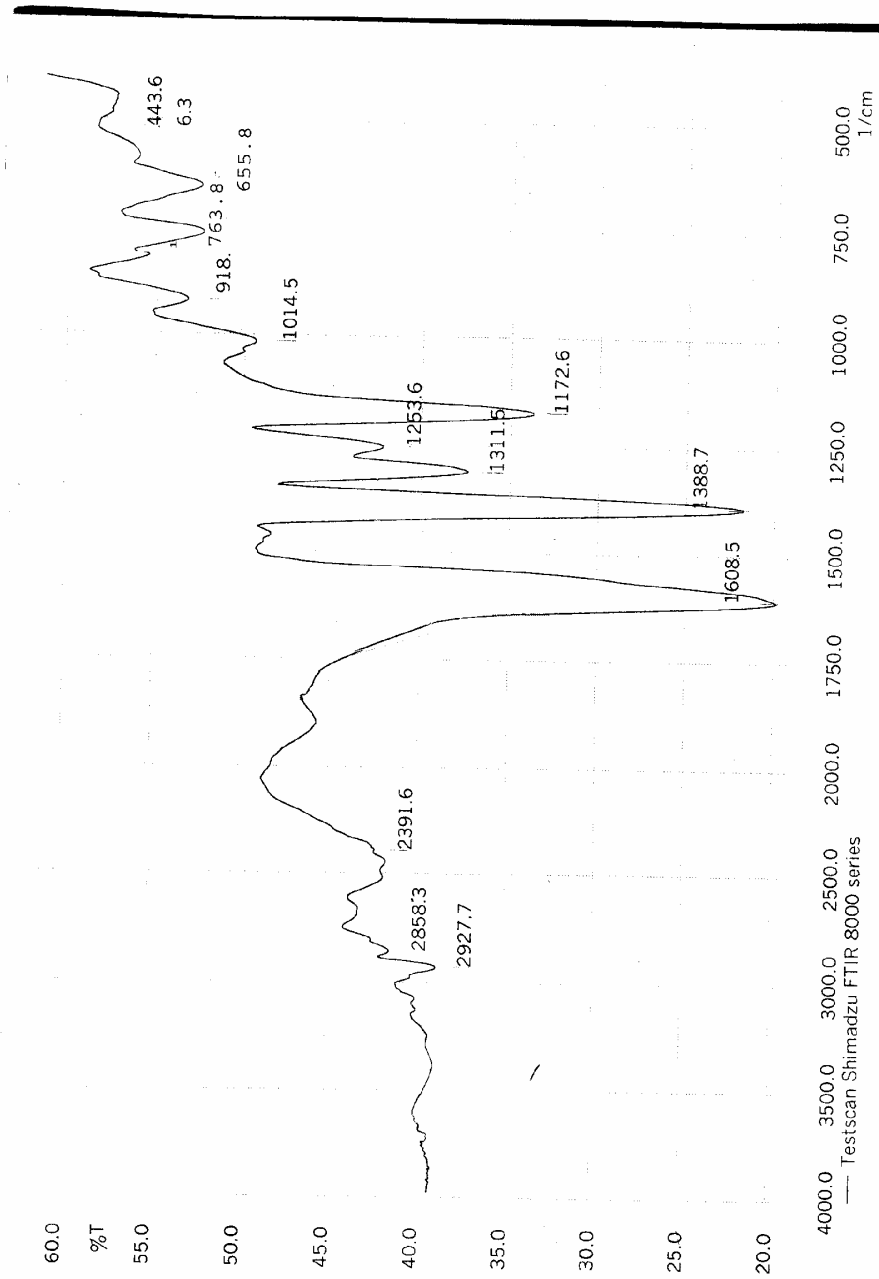


Figure (3-22) F.T.IR spectrum of magnesium adipate

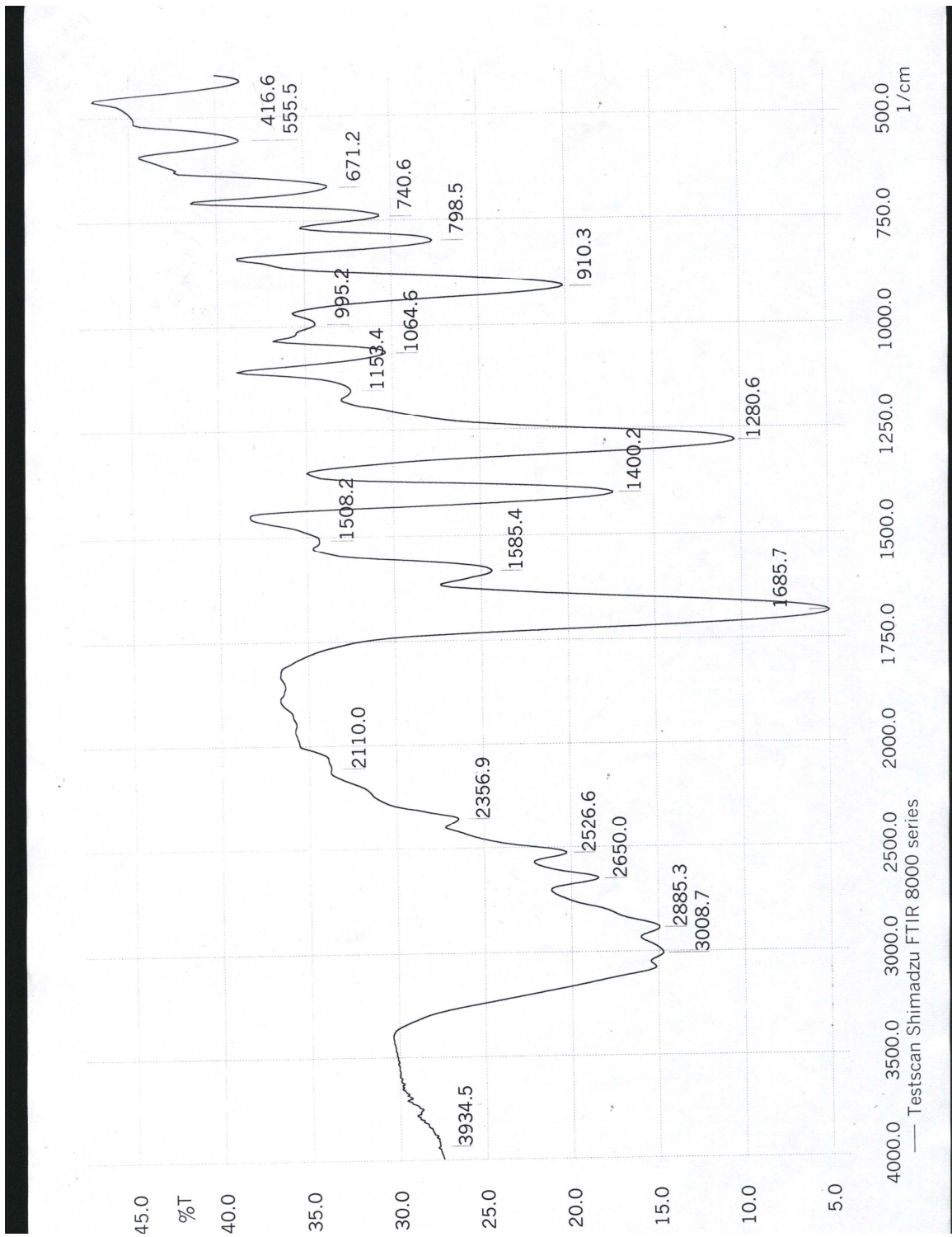


Figure (3-23) F.T.IR spectrum of phthalic acid

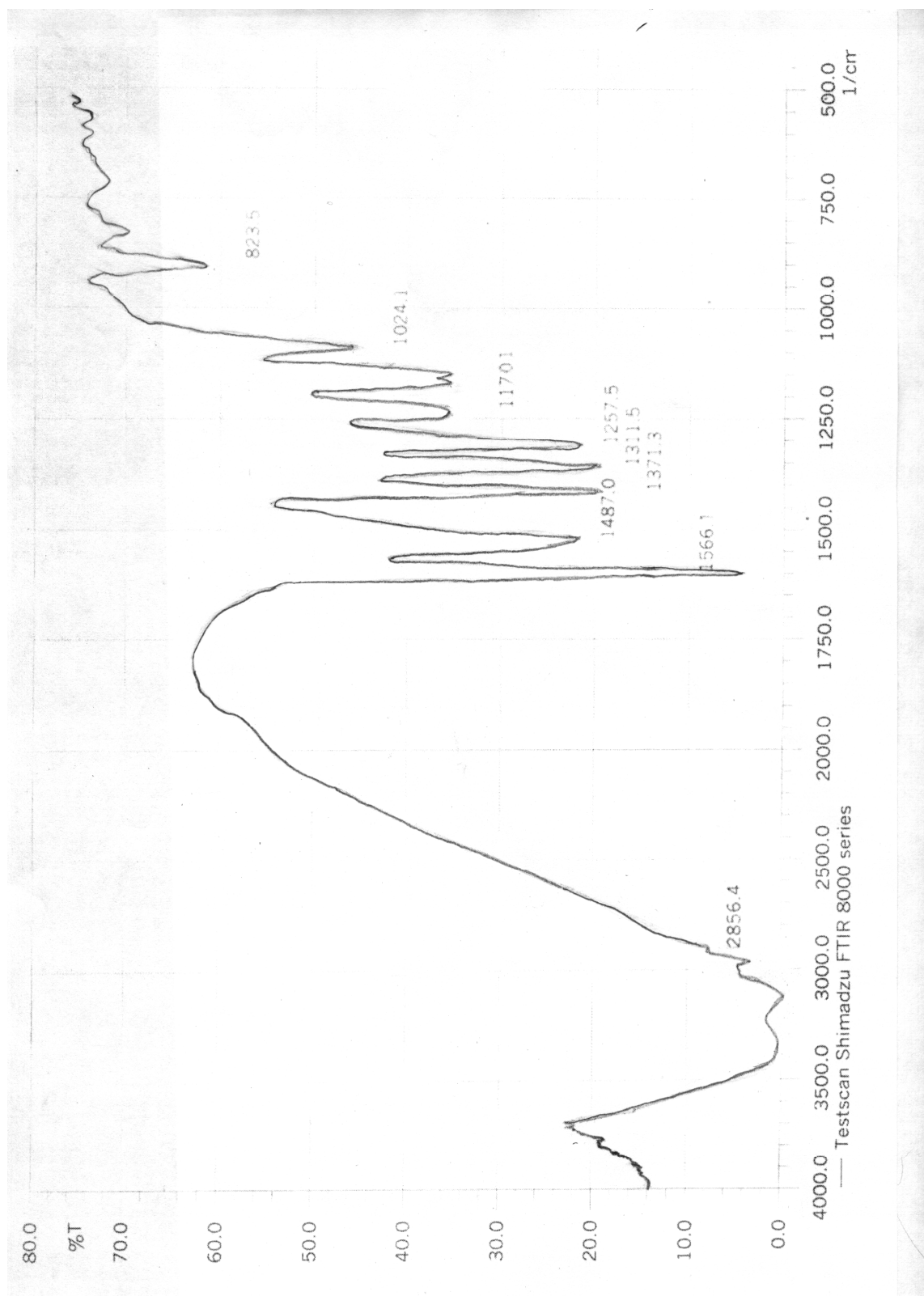


Figure (3-24) F.T.IR spectrum of magnesium phthalate

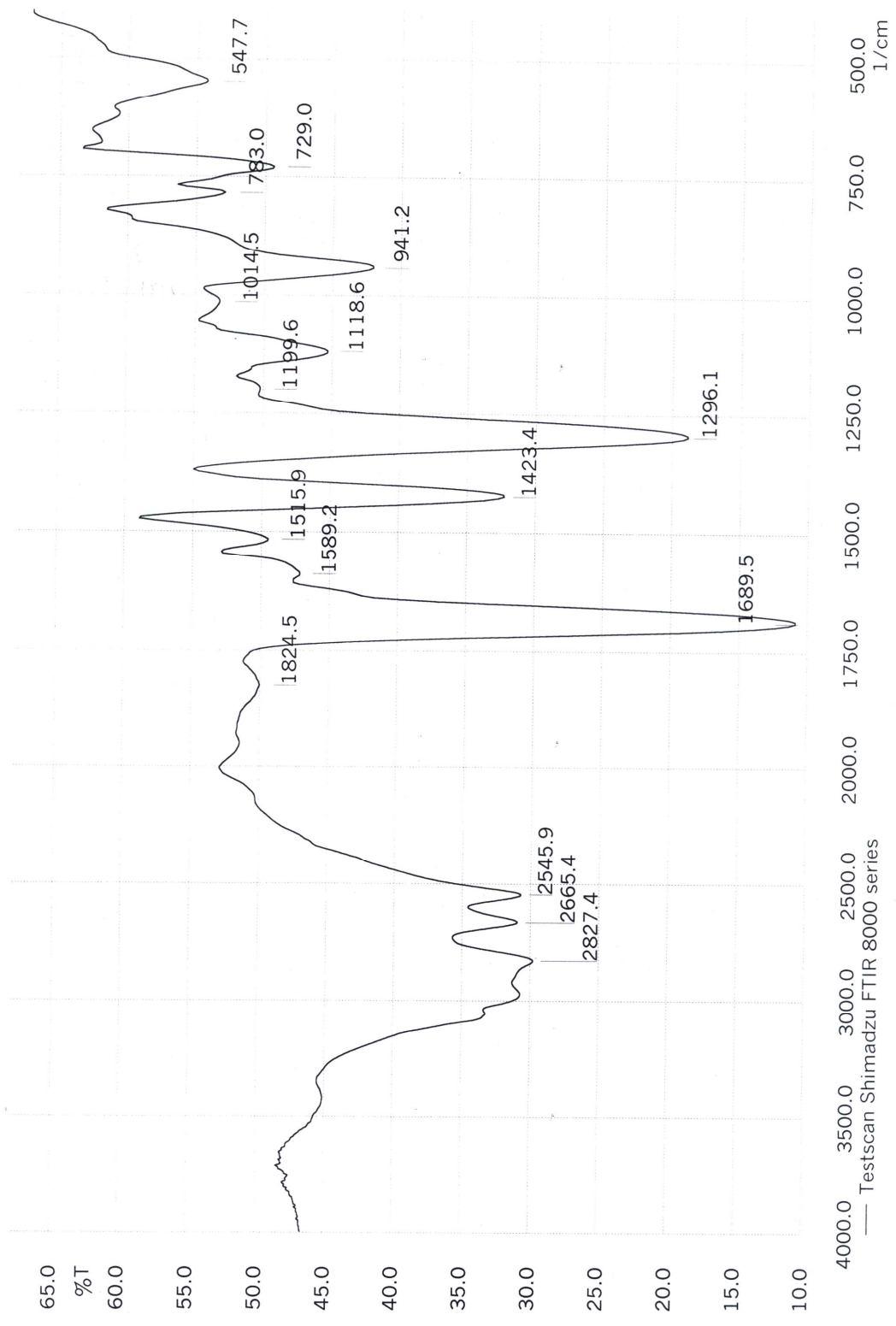


Figure (3-25) F.T.IR spectrum of terphthalic acid

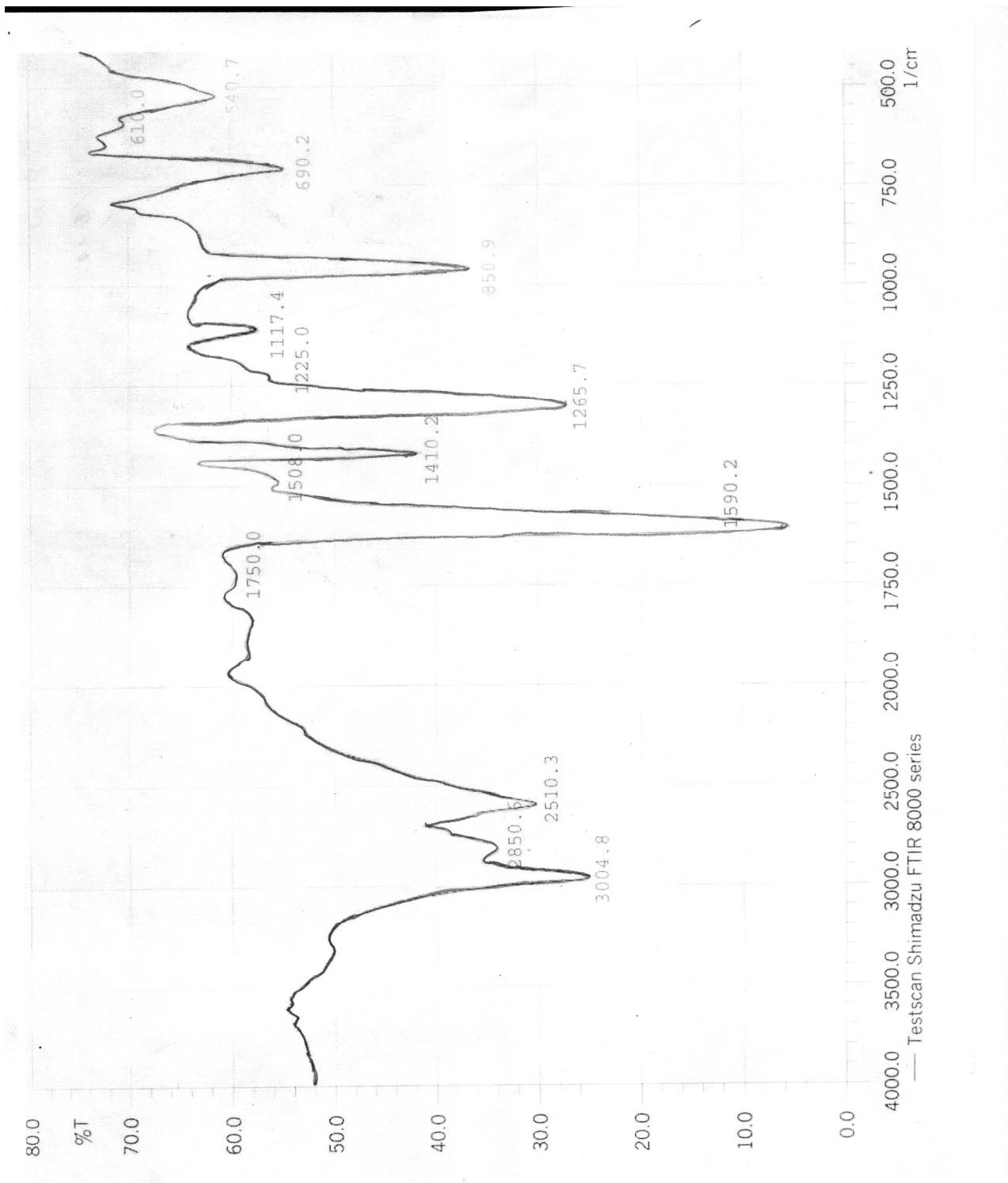


Figure (3-26) F.T.IR spectrum of magnesium terphthalate

compounds	O-H starchin g cm ⁻¹	C-H aliphatic Starchin cm ⁻¹	C-H Aromatic Starchin cm ⁻¹	C=O Starchin g cm ⁻¹	C-O Starchin cm ⁻¹	O-H Bending Out of plane cm ⁻¹
Lauric acid		2920.0a sym. 2850.6 sym.		1797,2	1122,0	937.3
Magnesium laurate		2923.9 asym. 2854.5 sym.		1081,0	1116,7	
Archedic acid		2916.2 asym. 2848.7 sym.		1695.3	1026,1	904,1
Magnesium arachidate		2920.0 asym. 2850.6 sym.		1573.8	1114.8	
Palmatic acid		2918.1 asym. 2848.7 sym.		1797,2	1103,2	941,2
Magnesium palmatate		2920.0 asym. 2850.6 sym.		1556.4	1112,9	
Sodium oleate		2925.8 asym. 2852.5 sym. 3005.0 olifene		1562.2	1130.0	
Magnesium oleate		3024.2 olifene 2923.9 asym. 2852.5 sym.		1093,1	1026,1	
Sodium stearate		2916.2 asym. 2848.7 sym.		1079,9	1110.9	
Magnesium stearate		2930.2 asym. 2850.6 sym.		1006,4	1112,9	
Phthalic acid		3008.7 asym. 2885.3 sym.	3100.0	1780,7	1074,0	910,3
Magnesium phthalate		2960.0 asym. 2856.4 sym	3090,0	1077,1	1024,2	
Terphthalic acid	3200	2980.3 asym. 2827.4 sym	3100,2	1689.5	1118,6	941,2
Magnesium terphthalate		2850.6sym.	3004,8	1090,2	1117,4	
Benzoic acid	3400,0	2930.5 asym. 2831.3 sym.	3104,9	1789,0	1122,0	929,6
Magnesium benzoate		2960.0asym. 2896.9 sym.	3000,0	1700,0	1040,3	
Cyclohexan carboxylic acid		2935.5 asym. 2862.2 sym.		1701,1	1029	940,1
Magnesium cyclohexan carboxylate		2942.3 asym. 2855.8 sym.		1093,9	1080,6	

Cinnamic acid	3020,6	2960.0 asym. 2827.4 sym. 3005.4 olifene	3100,0	1681,8	1083,9	968,2
Magnesium cinnmate		2931.6 asym. 2869.9 sym.		1608,0	1047,3	
Adipic acid	3433,1	2927.7 asym. 2858.3 sym.		1700,0	1190,6	960,3
Magnesium adipate		2927.7 asym. 2858.3 sym.		1608,0	1172,6	

3.3 Magnesium sulfonate :

The sulfonic acid used in this work was the commercially available one, which is used liquid detergent industry. This commercial acid may be a mixture of alkane, aromatic, and /or alkaryl oil soluble sulfonic acid. The dark sulfonic acid was converted first to it's light brown sodium salt using sodium hydroxide, which was used to get the magnesium sulfonate of a light yellow oily liquid, this crude product was suitably treated to get a pure magnesium sulfonate.

It was found the prepared magnesium sulfonate was highly soluble in xylene, toluene, and gas-oil. The metal content of the complex was determined and found to be 4.15 % .

Because magnesium sulfonate are both water and oil soluble with appreciable metal content, it can be used as surfactant in the production of an overbased magnesium

3.4 Magnesium emulsion :

Magnesium emulsion additives which is obtained by mixing heavy oil and water together in the presence of a surfactant. It was prepared following two routes: in the first route heavy oil(50 ml), containing essentially an aqueous solution of one water soluble metal salt selected from the halides of magnesium (10 ml of saturated solution of magnesium chloride) and 0.5gm of sodium laurel sulfonate as a surfactant. In the second route from the magnesium acetate solution (5.0gm of magnesium acetate in 10 ml water)was mixed with 10 ml crude oil using magnesium sulfonate as a surfactant(0.2 gm).

Oil-water separation of the resulting emulsion did not take place and the emulsion state was maintained even at temperature range (0- 100 C°). The metal content of the emulsion solution obtained by following first route was (8.5% Mg), while it was (13.5% Mg) in the emulsion of the second route, the later percent was obtained from two sources ,i.e. (9.35% Mg) from the magnesium acetate and (4.15% Mg) from the surfactant; therefore the magnesium sulfonate, prepared as described in section two is preferred since it gives higher metal content.

The amount of metal salt employed will vary with the particular metal and salt chosen, with the surfactant selected, with the particular heavy oil and fuel burning equipment being treated, and will depend upon whether or not two or more metal salts are utilized together in one aqueous solution⁽⁷⁰⁾. It is an advantage of the aqueous solution heavy fuel oil additives that they permit relatively high concentrations of the metal salts in aqueous solution, and yet afford good stability in use. The economic benefits attendant the use of products with relatively high concentrations of active ingredients is well recognized⁽⁷¹⁾. The magnesium emulsion are characterized by improved stability, and was proved to be stable at temperatures range (0–100).

One of combustion technologies which was developed an oil-water emulsion additive in which oil is mixed with water. This oil-water emulsion additive has an improved combustion efficiency because water particles micro-explode due to the discrepancy of the boiling points between heavy oil and water (b.p. of heavy oil is 300 C° or more, b.p. of water is 100 C°) so that the explosion divides the oil into finer particles and it leads to promotion of diffusion combustion when the emulsion fuel is sprayed into combustion chamber having high temperature⁽⁷²⁾. The mixing ratio of water to oil should be changed and the amount of addition of magnesium salt should be naturally changed. For example, in the paragraph (2.6.1) where 1 weight part of water(10 ml) to 5 weight parts (50 ml) of crude oil was used, about 5 g of magnesium chloride was added, and in paragraph (2.6.2) where 1 weight part of water (10 ml) to 1 weight parts (10 ml) of crude oil was used, about 5.0 g of magnesium acetate was added. As it is clear from above examples, the more inorganic components is needed as the higher ratio of the amount of water to the amount of crude oil is used so that the stabilization of emulsion state is designed. And the amount of magnesium salts depend on the various combination of the water and oil mixture. It was confirmed that the water particles are covered with thin film and are capsulized by oil. This is the phenomenon that a film is formed on the surface of water particle and the water particle is capsulized by oil as a result of the reaction among the components contained in crude oil⁽⁷³⁾. While this fuel additive was boiled under atmospheric pressure, it kept a boiling point of additive 100 C° , and when heating was stopped and the temperature fell to the room temperature ($25\text{-}30\text{ C}^\circ$), the oil-water separation was not occurred and any change in the capsule was not observed. Further, after the fuel of the room temperature was transferred into the room of -5 C° and was kept there for one week, it was

transferred back to room temperature. After two days, the situation was the same as described above.

. Each three pieces of iron nail as the specimen was put in three separate vessels containing the fuel of the present study, heavy oil and water each, and after every one week the degree of corrosion was estimated by visual observation. With nails in the vessel containing water, oxidization phenomenon became clear after 2 weeks and all of three nails were wholly oxidized when 5 weeks passed. With nails in the vessel containing heavy oil, oxidization phenomenon was not observed even after half an year. With nails in the vessel containing the present fuel, the situation was the same as nails in heavy oil. The results of the corrosion in water and in heavy oil was reasonable, but it is natural to be considered that in the fuel of the present study nails would contact with the water particles in the fuel and would be partly oxidized. But as described above, the water particles in the fuel are capsulated by chemical reaction and in this situation the water particles do not come out to the surface. Thus water does not contact to not only vessel wall but also the surface of nails and therefore nails would be never oxidized to corrosion.

Magnesium emulsion additives can retain the very strong emulsion state by the addition of magnesium salt of the inorganic components and surfactant, and the cohesion among water particles does not occurred in any change of temperature and the water particles can retain a constant size⁽⁷²⁾. Therefore the fuel do not bring about oil-water separation and each particle of water is contained in oil without changing from a heating stage to burner spraying stage, and the ideal micro explosion occurs, surrounding oil drops are divided to super fine particles and the evaporation of oil is accelerated and mixing with air is accelerated so that the diffusion combustion is promoted. As the result, a good condition for combustion is prepared and a stable high

temperature is maintained in the inside of the combustion chamber⁽⁷⁰⁾.

Conclusion

Taking in account the results of the present work, the following conclusion can be made:

- 1-The oleate complex of magnesium was found to have the highest oil solubility among the carboxylates derivatives with magnesium content of 3.52% .
- 2- The prepared magnesium sulfonate have 4.15% metal content with very high oil solubility.
- 3- The magnesium complex of sulfonate has higher oil solubility and metal content than it's analogue of carboxylates.
- 4- It was found that the method followed to prepare the magnesium emulsion using magnesium sulfonate as surfactant gave higher metal content (13.5 %) than the product obtained using sodium laural sulfonate as surfactant (8.5 %), with no problems of oil solubility.
- 5- The emulsion formulations was found to be more suitable as oil additives than the formulations obtained using the soluble products with respect to the higher metal content and good stability in the oil.
- 6- The metal content of the emulsion additives can be increased by increasing the water content with respect of the total volume.
- 7- Generally it can be shown that a wide variety of additive formulations have been presented with varying degree of solubility and metal content, the choice among them can be judged depending on the user requirements.

Suggestions for future work

1-Due to the unavailability of the technique required to study the effectiveness of the prepared magnesium complexes, it is of great importance to test their effectiveness as corrosion inhibitors using small oil burning unit.

2- In order to have higher metal content by using metal oxide or salts, a particle size reduction technique has to be used to get a nanoparticale size of these compound to obtain miscible oil mixture.

3- Preparation of overbased magnesium carboxylates and sulfonates.

4- Preparation of other metals derivatives, i.e. Fe, Cr, or Silicon.

5- Preparation of a combination of two metal additive.