جمهورية العراق
وزارة التعليم العالي و البحث العلمي
جامعة كربلاء
كلية التربية للعلوم الصرفة
قسم الكيمياء

تحضيرو تشخيص بعض مركبات الكبريت غير متجانسة الحلقة و دراسة تأثيرها كمثبطات لهب لراتنجي البولي استر غير المشبع و الأيبوكسي

هذه الرسالة مقدمة الى
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من قبل

حنان قيس سعدون المسعودي

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إشراف
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Republic of Iraq
Ministry of Higher Education
& Scientific Research
University of Karbala
College of Education for Pure Science
Chemistry Department

Preparation and Characterization of some hetero cyclic sulfur compounds and studies its effect as flame retardant for unsaturated polyester and epoxy resins

A Thesis
Submitted to the Council of the College of Education for Pure Sciences–
University of Karbala, in Partial Fulfillment of the Requirements for the
Degree of Master in Chemistry Sciences

By

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September ⁄ 2017 AC　　　**Thi al-Hijjah ⁄ 1438 AH**

بسم الله الرحمن الرحيم

وَمَن يَتَّقِ ٱللَّهَ يَجعَل لَّهُ مخرَجاً ﴿ ٢ ﴾ وَيرزُقهُ
مِن حَيثُ لَا يَحتَسِبُ وَمَن يَتَوَكَّل عَلَى
ٱللَّهِ فَهُوَ حَسبُهُ إِنَّ ٱللَّهَ بَٰلغ أَمرِةِ قَد جَعَلَ ٱللَّهُ لِكُلِّ
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صدق الله العلي العظيم

سُورَةُ الطَّلَاقِ(٢-٣)

Dedication

I would like to dedicate this work to

My father, who presented me great support during my study

My mother, who kept on supporting and assisting me.

My brothers, sisters and their families.

Hanan

ACKNOWLEDGMENTS

First of all, praise is to God, who enabled me to overcome all the difficulties associated with this study till producing the thesis in its final form.

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My thanks gradual to all the staff members of the department of chemistry, specially, Prof. Dr. **Hamieda Edan Salman**

I would like to express my sincere appreciation to all my friends, Finally, many thanks go to those whom I haven't mentioned.

Hanan

Supervisor Certification

I certify that this thesis (**Preparation and Characterization of some hetero cyclic sulfur compounds and studies its effect as flame retardant for unsaturated polyester and epoxy resins**) was papered under my supervision in the chemistry department-College of Education for Pure Sciences, University of Karbala, in partial Fulfillment of the requirements for the degree of Master in Chemistry Sciences by the student (**Hanan Qais Saadoun**).

Signature:
Assist. Prof. Dr. **Mohammad Nadhum AL-Baiati**
Supervisor
Date: / 9 /2017

In view of the available recommendations, I forward this thesis for debate by the examining committee.

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Name: Prof. Dr. **Hamieda Edan Salman**
Date: / 9 /2017
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This is to certify that I have read the thesis entitled (**Preparation and characterization of some hetero cyclic sulfur compounds and studies its effect as flame retardant for unsaturated polyester and epoxy resins**) and corrected the grammatical mistakes I found . The thesis is, therefore, qualified for debate .

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Name:

Date: / / 2017

Committee Certification

We certify that, we read this thesis **(Preparation and characterization of some hetero cyclic sulfur compounds and studies its effect as flame retardant for unsaturated polyester and epoxy resins)** and as examining committee examined the student (**Hanan Qais Saadoun**) in its content, and that in our opinion it is adequate (**Excellent**) with standing as a thesis for degree of master in chemistry sciences.

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Name: Assist. Prof. Dr. **Mohammad N. AL-Baiati**
Date: / /2017
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Abstract

In this study, ten heterocyclic organic compounds were prepared and characterization by ^{1}HNMR, ^{13}CNMR, FT-IR and CHN . They were studied on effectiveness in inhibiting the flame and increasing the resistance to ignition of the unsaturated polyester and epoxy resins, and these additives are:

1. Additive A1: (5,6-diphenyl-6H-1,3,4-thiadiazin-2-amine)

2.Additive A2:(Pentane-2,3,4-trione3-[(5,6-diphenyl-6H-1,3,4-thiadiazin -2-yl)hydrazine])

3. Additive A3: (5-[(z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-4,6 dimethyl-2H-1,3-thiazin-2-amine)

4. Additive A4: (6-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-5,7 dimethyl -1,3,4-thiadiazepin-2-amine)

5. Additive A5: (5,6-diphenyl-2-[(Z)-(2,4,6-trimethyl-2H-1,3-thiazin-5-yl) diazenyl]-6H-1,3,4-thiadiazine)

6. Additive A6: ((4Z,6E)-6-((Z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl) diazenyl)-5,7-dimethyl-2,3-dihydro-1,4-thiazepine -3-carboxylic acid)

7. Additive A7: (5-(1,4-phenylene)bis (1,3,4-thiadiazinol-2-amine)

8. Additive A8: (2,2-(1,4-phenylene-bis-(1,3,4-thiadiazole)-5yl)bis(1,2-benzisothiazol-3(2H)-one) 1,1,1,1,-tetraoxide)

9.Additive A9: (2,2-(1,4-phenylene)bis(4,5-dihydro-1,thiazole-4-carboxylic acid)

10. Additive A10: (5,5-[1,4-phenylene bis(4,5-dihydro-1.3-thiazole-2,4-diyl) bis (1,3,4-thiadiazol-2-amine))

Three sheets in three dimensions (13 x 13 x 0.3 cm) of unsaturated polyester and epoxy resin with the above additives were prepared with the weight percentages (0.2, 0.4, 0.6 and 0.8%) and these sheets were cut according to the (ASTM) standards .

The study included a series of standard tests used to measure the obstruction of the flame and increase the resistance of ignition. Two standard methods were chosen to demonstrate the efficiency of the additives in blocking the abrasion of the unsaturated polystyrene resin and the epoxy resins.

1. Method of measuring the limiting oxygen index (LOI) using the approved method of testing (ASTM: D-2863).

2. The method of measuring the rate of burning (R.B), the extent of burning (E.B) and the time of burning (TB) through the approved method of examination (ASTM: D-635).

The results of the above measurements showing that the additives referred to the above were significant effectiveness in inhibition of the flame and increased the ignition resistance of unsaturated polyester resin and epoxy resins. The efficiency of additives was ordered as.

A10 > A4 > A8 > A3 > A7 > A6 > A5 > A2 > A1 > A9

The study was showed that a good flame retardant and obtained in all percentages of additives of obtained a self-extinguishing in percentage 0.2% for each additives A4 and A10, self-extinguishing in percentage 0.4 % for the additives A3 and A10, and Non-Burning occurring in the percentage 0.4 % for the additives A4 and A10, so the percentage 0.6% for the additive A8 for Polyester resin also 0.6 % for the additives A4 and A10 for epoxy resins.

List of abbreviations

Code	Name
R.B	Rate of Burning
LOI	Limiting Oxygen Index
^{13}C-NMR	Carbon nuclear magnetic resonance
^{1}H-NMR	Proton nuclear magnetic resonance
DMSO	Dimethyl Sulfoxide
ASTM	American Section of the International Association for Testing Material
FT-IR	Fourier Transformer Infrared Spectroscopic
M.F	Molecular Formula
F.R	Fire Requires
S.E	Self- extinguishing
TLC	Thin Layer Chromatography
ATM	Average time of burning
NB	Non- burning
AEB	Average Extent of Burning
MEKP	Methyl ethyl ketone peroxide
C.H.N	Element Analysis Instrument

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CHAPTER ONE

Introduction

1- INTRODACTION

1.1 History of heterocyclic chemistry

The history of the heterocyclic chemistry is beginning in the 1800s, as step with the development of the organic chemistry. Some notes worthy development [1]. In 1818s, Brugnatelli isolate alloxan from the uric acid; In year 1832s, Dobereiner was produce furfural by the treating starch with sulfuric acid; In year1834s, Runge [2]was obtaining pyrrole (fiery oil) by drying distillation of the bones; In year1906s, Friedlander aimed to synthesis indigo dye , allowing to synthetsis chemistry to displace the large agricultural industry. In year 1936s, Treibs[3]aimed to isolate chlorophyll derivatives from the crude oil and explaining the biological origin of the petroleum; In 1951s, Chargaff's rules were described ,highlighting the role of heterocyclic compound (purines and pyrimidine) in the genetic code [3].

1.2 Heterocyclic compounds

Heterocyclic chemistry is the branch of the organic chemistry that dealing with the synthesis, properties and application of these heterocyclic [4]. Heterocyclic compound or ring structure is a cyclic compound that has atoms of at least two different elements as members of its rings [3].

Examples of heterocyclic compounds were included all the nucleic acid, the majority of drugs, most biomass (cellulose and related materials), and many natural and synthetic dyes [5].

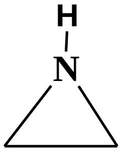
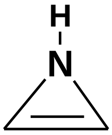
1.3 Classification of heterocyclic compounds

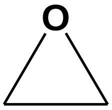
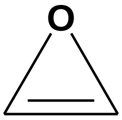
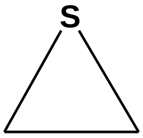
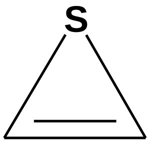
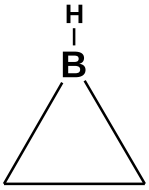
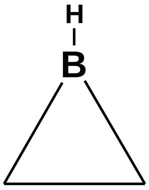
Although heterocyclic compounds were inorganic**,** most contain at least one carbon, while the atoms that were neither carbon nor hydrogen were normally referred to the in organic chemistry as hetero atom, this is usually in comparison to all –carbon backbone [6].

The Heterocyclic compounds can be classified as based on their electronic structure. The saturated heterocycles behave like the acyclic derivatives, for the examples piperidine and tertrahydrofuran were conventional amines and ethers, with modified steric profiles. Therefore, the study of the heterocyclic chemistry focused especially on the unsaturated derivatives, and the preponderance of work and application involve unstrained 5- and 6- membrane rings. Including pyridine, thiophene, pyrrole and furan. The unsaturated rings can be classified according to the participation of the heteroatom in the pi system [7].

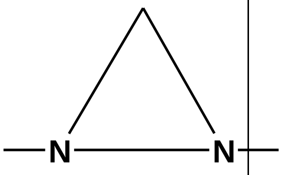
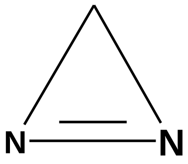
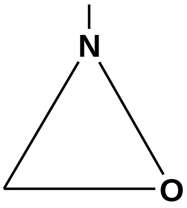
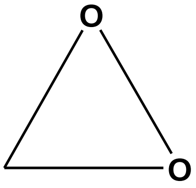
1.3.1 Three-member rings

Heterocyclic with three atoms in the ring are more reactive because of ring strain. Those containing one heteroatom are, in general, stable. Those with two hetero atoms are more likely to occur as reactive intermediate common 3-membered heterocyclic with one heteroatom [8].

Heteroatom	Saturated	Structure the ring	Unsaturated	Structure The ring
Nitrogen	Aziridine		Azirine	

Oxygen	Oxirane		Oxirene	
Sulfur	Thiirane		Thiirene	
Boron	Borirane		Borirene	

Those with two heteroatoms include:

Heteroatom	**Saturated**	**Structure the ring**	**Unsaturated**	**Structure the ring**
Nitrogen	Diziridine		Diazirine	
Nitrogen/Oxygen	Oxaziridine		—	
Oxygen	Dioxirane		—	

1.3.2 Four- Member Ring

In the four – membered heterocyclic [9], the ring strain was less than in the corresponding the three –membered ring compound and was approximately equal to that found in cyclobutane. Examples of the four membered heterocyclic compounds were shown as in the figure (1-1).

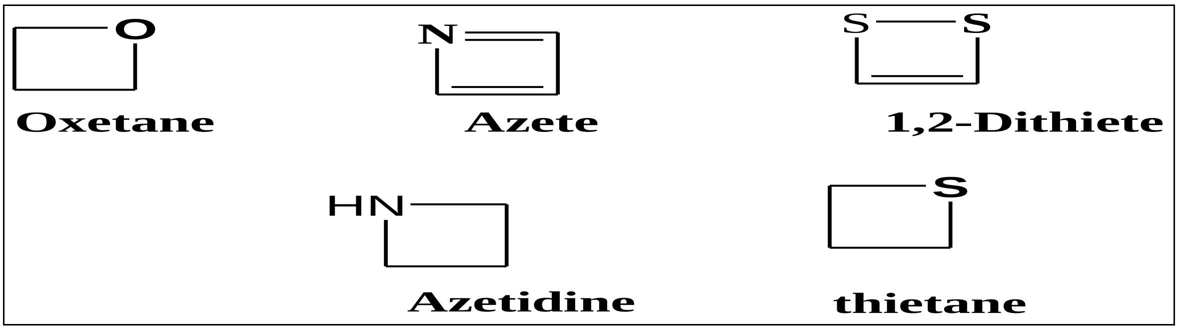


Figure (1-1): Four membered heterocyclic compounds

1.3.3 Five – Member ring

This class was representing large group of the heterocyclic. The ring strain was no important rather than in the three and four – membered heterocyclic. The examples for the five membered heterocyclic with oxygen, sulfur, nitrogen, phosphor and selenium atoms were shown as in the figure (1-2) [10].

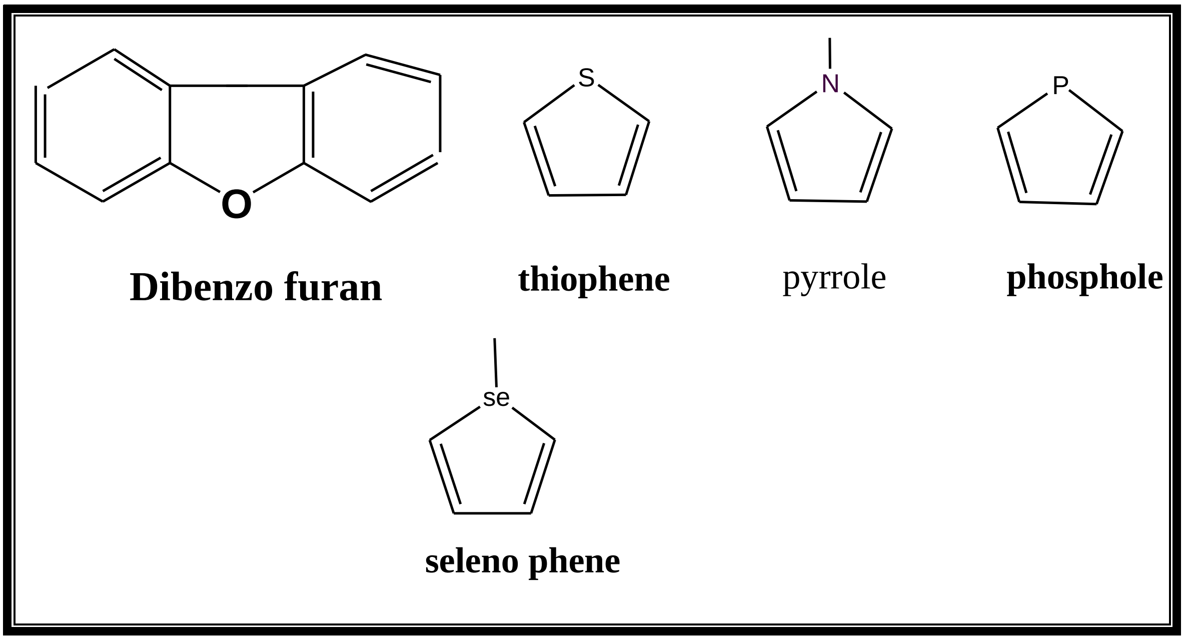
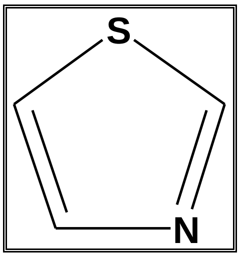


Figure (1-2): five – Membered ring

1.3.3.1 Thiazole

Thiazoles were a class of organic compounds that related to azoles with a the common thiazole functional group. Thiazole was aromatic heterocyclic organic compound that has a five-membered molecular ring structure, C_3H_3NS. The thiazole moiety was apart of vitamins B_1 (thiamine) and epothilone, benzothiazole as animportant thiazole examples eluciferin . The thiazole have been used to give N-S free carbenes. The amino atom can be alkylated to create the thiazolium cation [11] .



Figure(1-3): The structure of Thiazole

1.3.3.2 Thiadiazoles

The thiadiazoles are five-membered unsaturated ring structure composed of two nitrogen atoms and one sulfur atom. There are four isomeric types: 1,2,3-thiadiazole; 1,3,4-thiadiazole; 1,2,4-thiadiazole and 1,2,5-thiadiazole [12] .

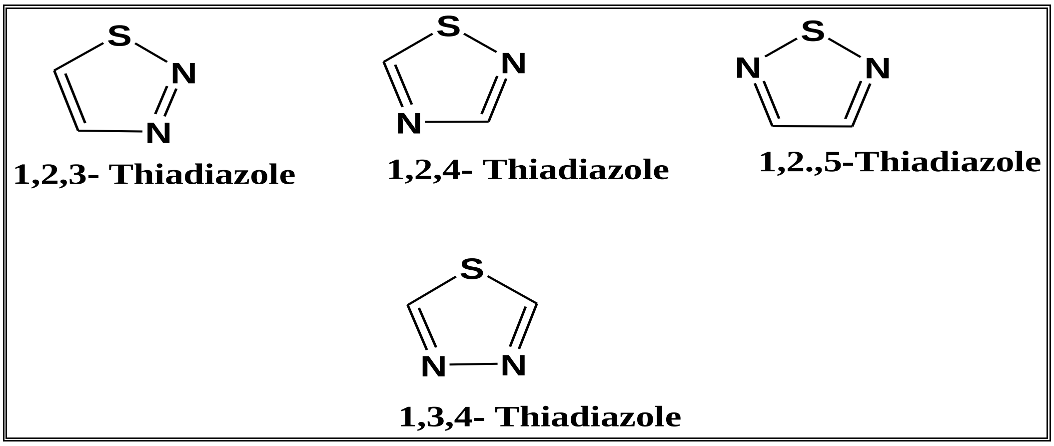


Figure (1-4): Isomers Structure of Thiadiazole

1, 3, 4-thiadiazole moiety in which the sulfur present at position-1, and the two nitrogen atom at the position-3 and the position-4, is an important class of heterocyclic compounds that exhibit diverse applications in anorganic synthesis, pharmaceutical and biological applications. Among them 2,5-disubstiuted-1,3,4-thiadiazoles were associated with the divers of the biological activities were probably by the virtue (-N=C-S) grouping [13]. 1, 3, 4-thiadiazole derivatives were possessed as awide range of the therapeutic activities [14].

1,3,4-thiadiazole[15-19] and their derivatives were exhibit as awide range of pharmacological activity such as antimicrobial activity, anti-inflammatory, antibacterial, anti-biotic, anti-fungal, anticancer activity, such as shown in the Figure (1-5) .

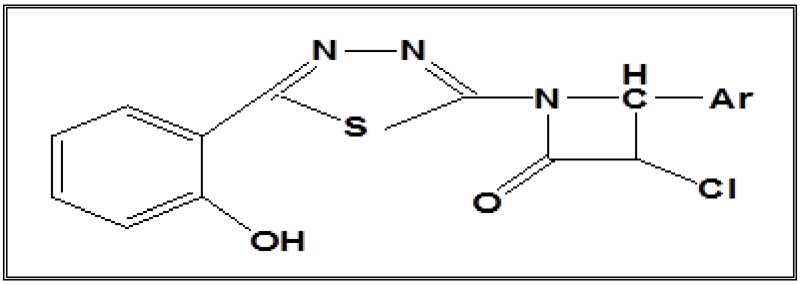
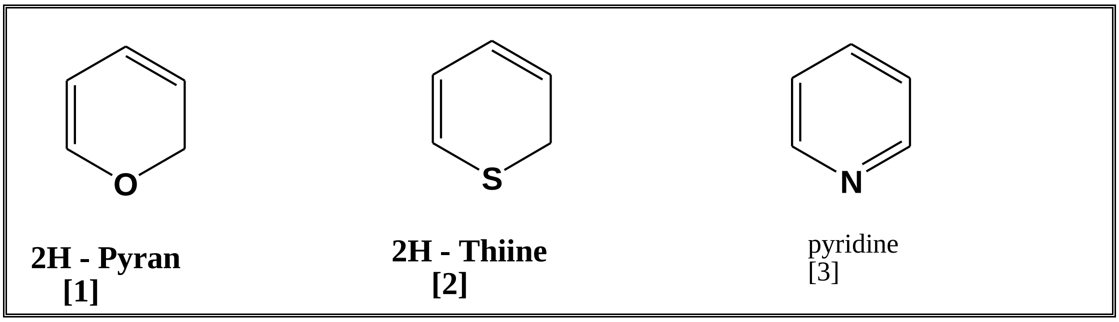


Figure (1-5): Derivatives of 1, 3, 4-thiadiazole.

Thiadiazoles were clear to be yellowish liquids which were soluble in the alcohol, ether and slightly soluble in water; Thiadiazoles were starting the material for the numbers chemical compounds including the sulfur drugs [20]. Thiadiazoles were easily metabolized by biochemical reactions and Thiadiazoles were non-carcinogenic in nature [21]. 1, 3, 4-thiadiazole was relatively stable in the aqueous acid solution but the nucleus can undergo ring cleavage by the aqueous bases solution [22] .

1.3.4 six-membered ring

The ring strain was in six-membered heterocyclic was alittle or non importance. pyran[1], thiine[2] and pyridine[3], with oxygen, sulfur and nitrogen atoms were examples for the six-membered heterocyclic, as shown in the figure (1-6) [23].



2H - Pyran [1]

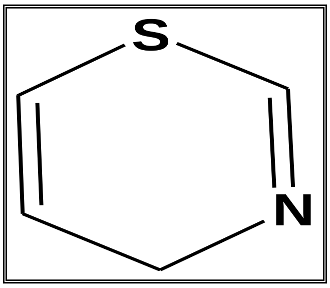
2H - Thiine [2]

pyridine [3]

Figure (1-6): The structure of pyran [1], thiine [2] and pyridine[3].

1.3.4.1 Thiazine

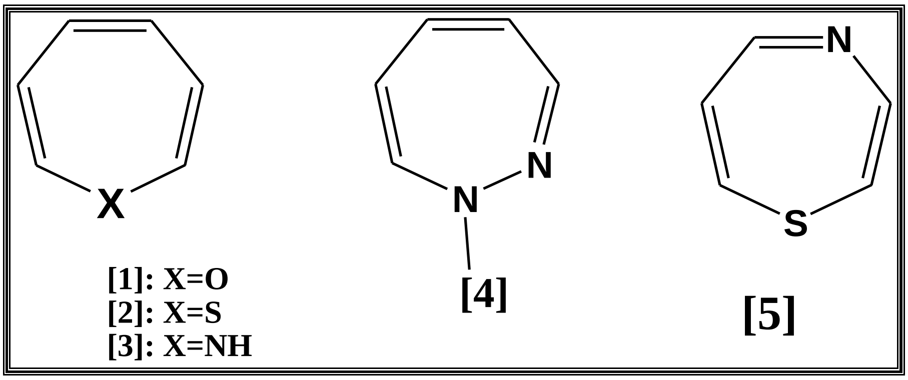
Thiazines were represented as an important class of the heterocyclic compounds due to their valuable biological properties [24]. For the examples, some derivatives of thiazine were cannabinoid receptor agonists, also Thiazines can be acted as an anti-hypotensive, anti-tubercular and anti-bacterial agents. Thiazine derivative can be used for gastrointestinal disorders or diabetes prevention [25].The Condensation of the heterocyclic systems possessing thiazine ring have been reported as anti-oxidant, analgesic, anti-inflammatory agents, or calcium channel modulators [24]. Thaizines were useful intermediates in synthetic organic chemistry [25].



Figure(1-7): The structure of Thiazine ring

1.3.5 Seven-membered ring

Heterocyclic seven – membered rings were constituted the core or a key fragment of the number of abioactive compounds [26]. Oxapine [1], thiepin [2], azepine [3], diazepine [4], thiazepine [5] are examples for a seven – membered heterocyclic compounds, as shown in the figure(1-8) [27-31].



[1]: X=O
[2]: X=S
[3]: X=NH
[4]
[5]

Figure (1-8): Structures of oxapine [1], thiepin [2], azepine [3], diazepine [4], thiazepine [5].

1.3.5.1 Tiazepine

Thiazepine [32] moieties were represented as an important class of seven – membered heterocyclic compound that having Nitrogen and Sulphur as hetero atoms in their chemical structure' figure (1-7) [33]. Thiazepines were a privileged structure because of its presence in the number of pharmacological important compounds and also present in awide range of the rings of natural and synthetic biologically active agents [30]. Thiazepines were considered as one of the drugs which have biological interest due to their activity on the central nervous system, as muscle relaxant, enzyme inhibitors, anticonvulsant, anticancer and other uses [33].

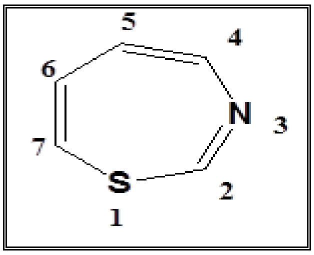


Figure (1-9): Structure of 1, 3-Thiazepine

1.4 Flame retardant composite

1.4.1 Burning Basics

Fire requires (F.R), four major components such as the fuel, heat, oxygen, and a sustainable chain reaction for the initiating of the fire, such as in the figure (1-10). Fire requires (F.R), were used as a different mechanisms to interrupt the cycle by acting indifferent stages of fire [34].

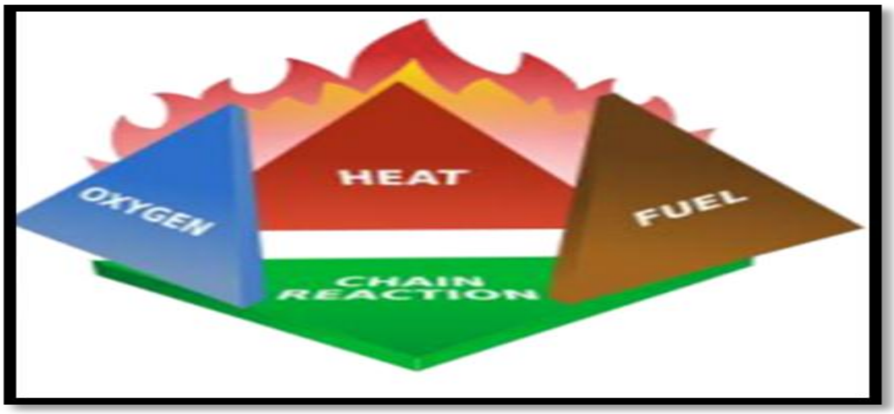


Figure (1-10): Basic for burning

1.4.2 Additives or Fillers

They were usually solid materials that were added to the polymer compositions to transform or develop a number of physical, mechanical, electrical, and other properties were required to be the new polymer use, or reduce of the cost of the polymer production. The term of filler is limited to materials were consisting of the separate minutes or Fibers were not more than a few inches as along and the efficiency of fillers were depended on their physical properties such as particle size, structure, and proportions. The number of benefits of using additives can be identified as follows [35]:

1. Reduce cost of polymer (the resulting materials).

2. Reduce shrinkage resulting during polymerization process.

3. Reduce the temperature emitted during the masking.

4. Increasing the temperature for Distroption Temperature in the polymer.

5. Change some of the polymer properties (electrical, mechanical .... etc).

6. Minimize polymerization of polymers and liquids.

7. Increasing the stiffness of the polymer and the strength and stability of the dimensional dimensions of the stability of the product.

8. The properties were required for a particular use depending on the type of additives.

1.4.3 Flame resistance

The over of the past few years, polymeric materials were developed very in awide applications, with the using of these materials and composites extending to the most aspects of life [36]. This rapid was spread and deployment as an exceptional phenomenon that indicates the continued and increased use of these substances in the future [35]. Some of these applications include the exposure to the risk of Ignition or fire with adequate heat or heat source, and sufficient oxygen to the air, which increased the risk of fire as a resulting in the need for materials that reduce the ignition of these substances. The rate of combustion varies from polymer to another [37]. This difference is may be depend on the degree to which the polymer material is exposed to the ignition source [36].

The process of burning polymeric materials with the thermal source and sufficient amount of atmospheric oxygen involves a series of physical and chemical changes that occur for both polymer and ocean. figure (1-11) represents the polymer combustion cycle [38]:

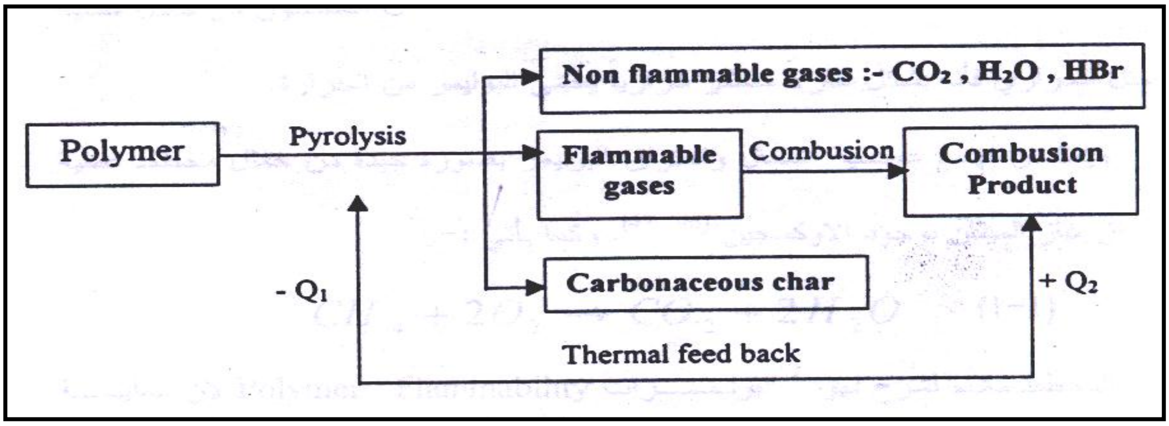


Figure (1-11): The polymer combustion cycle.

The cyclic plan has mainly in a two sequential processes:

Decomposition and Combustion, Both processes were associated with Ignition and Thermal Feed Back. The process of mug and ignition controls three pyrolysis products:

1. Non Flammable Gases.
2. Flammable gases.
3. Carbonaceous Char.

The energy consumed is during the thermal decomposition (- Q1) of expressed as the value of (+ Q2) which is the amount of heat generated during the combustion process. Non-flammable gases reduce volatile flammable materials and provide an inert atmosphere that forms a gas barrier between oxygen and the burned area. Coal, formed by the process of thermal decomposition, is a thermally stable insulator that protects the polymer from heat [38].

The process of ignition and combustion of polymer can be well understood by equating methane combustion with oxygen [39] as follows (equation-1):

$$\mathbf{CH_4 + 2O_2 \xrightarrow{\text{flame}} nCO_2 + n\text{-}1H_2O + \quad \Delta H \text{ ...... } 1}$$

It is also a suitable for the explaining polymer flammability because the combustion of most polymers involves the oxidation of hydrocarbons. The process of combustion gaseous fuels is generated by the thermal disintegration of polymeric material can be illustrated by the following formula (equation-2) [40]:

$$\mathbf{\text{Fuel gas} + O_2 \xrightarrow{\text{flame}} CO + CO_2 + ROH + RH + \text{Light} + \text{Heat} \text{ ......} 2}$$

Where RH and ROH represent incomplete combustion products and depend on the nature of the polymer material and the combustion environment [41]. In the addition of the oxygen methane combustion scheme can be used as a model for the complex polymer combustion process and also indicated that the combustion process involves a series of free-radical chain reactions which included the starting steps of Initiation and the growth of propagation and termination. Although different types of interactions occur during the combustion of polymeric material, the free radical reactions are prevailing and the mechanics of the following serial reactions illustrate (equation-3) [42].

$$\begin{array}{l}
\left.\begin{array}{l} O_2 \rightarrow 2\dot{O} \\ \dot{R} + \overline{R}H \rightarrow RH + \overline{\dot{R}} \end{array}\right\} \textbf{Initiation} \\[1em]
\left.\begin{array}{l} \dot{R} + O_2 \rightarrow RO\dot{O} \\ RH + \dot{O} \rightarrow \dot{O}H + \dot{R} \end{array}\right\} \textbf{Propagation} \\[1em]
\left.\begin{array}{l} \overline{\dot{R}} + \overline{\dot{R}} \rightarrow 2\overline{R} \\ RO\dot{O} + \dot{R} \rightarrow ROOR \end{array}\right\} \textbf{Termination}
\end{array} \qquad \textbf{......... 3}$$

The free radicals of the combustion process can be represented as follows (equations - 4&5) [41]:

Hydrocarbon Compound Fragment (RH) + $HO^{\cdot} \longrightarrow R+H_2O$ ……. 4

$$\begin{aligned}
&\dot{R}+O_2 \rightarrow RO\dot{O}\\
&2H\dot{O}+CO \rightarrow CO_2+H_2O\\
&\dot{H}+O_2 \rightarrow H\dot{O}+\dot{O}\\
&\dot{O}+H_2 \rightarrow H\dot{O}+\dot{H}
\end{aligned}$$

…….. 5

The free radicals ($HOO^{\bullet}$, $O^{\bullet}$, $HO^{\bullet}$, and $H^{\bullet}$) were the basis for the continued flame. Although most polymeric materials have self-resistance to combustion under certain conditions of heat and oxygen flow, to reduce the polymerization of polymers in general, chemicals have been used as flame-retardants and those substances either to be the additives, also called external flame retardants [42]. External-Flame Retardants, which were inefficient chemicals added and mixed with the polymeric materials without any chemical reaction. The most important qualities that must be characterized by these additives to obtain good flame impediments are as follows [43, 44]:

1. You should not interact with the main polymer chains and at the same time must be compatible without any conglomeration of additives.

2. The additives should be non-toxic and do not emit toxic or corrosive vapors during combustion.

3. The cheap price and easy to prepare.

4. It has no adverse effect on the physical properties of polymeric materials such as hardness, degree of deformation, etc.

5. The stable thermally and visually.

Examples of such additives are antimonytrioxide Sb_2O_3, chlorinated wax and phosphoric acid esters [44].

The other type of material used as flame retardants is an essential part of polymer synthesis. This is called internal flame retardants [45]. This type is characterized by its high efficiency because it a part of the polymer material composition after its interaction with it, for example, trichloroallylacetate, chlorostyrene, …, etc. [46].

The internal flame retardants are less commonly used than external flames because those were expensive and require complex techniques in their preparation process. Several studies [47] were reviewed to the subject of the polymerization. Those studies were confirmed in a three ways to reduce the polymerization of the polymers [48]:

1) The transform the polymer into a stable installation direction of heat and oxygen.

2) The polymer modification can be chemically modified to produce a low-flame polymer.

3) The polymer compounding can be installed with one or more flame impedances. This method has been widely used in commercial polymers.

1.4.4 The fire – retardants materials

The literature was referred to the using of a large number of chemicals as flame retardants to discourage the polymerization of various polymers [49]. Magnesium compounds such as magnesium hydroxide Mg $(OH)_2$ were be used in the inhibition of polypropylene with a 60% weight percentage and the magnesium carbonates that were used with the magnesium hydroxide [50]. The use of those compounds were required high concentration of 40-60% In order to be the efficient in inhibiting cirrhosis, and they have been used synergistically with many other compounds. Molybdenium Oxide MoO_3 [51] was used alone or in combination with the Sb_2O_3-MoO_3 antimony oxide Fe_2O_3 and magnesium oxide MgO [52] have been observed to the increase of the efficiency for phosphorus compounds in blocking cyanobacteria and reduce the density of smoke in polyolefins. So that, many types of compounds has been used as flame retardants. The following are the most important of these compounds.

The halogen compounds have been used alone or with the other compounds as flammable impediments and inhibition of polymerization. The efficiency of halogen compounds in blockage is directly dependent on the ease of halogen release. It has been observed that this efficiency is as follows: [53, 54]

$$I > Br > Cl > F$$

Fluorocarbons have been exclude for their inefficiency in flame retardation due to the high stability of the HF family. Iodine compounds have also been exclude despite their high efficiency due to their optical and thermal instability as well as their high cost. Concentration of chlorine and bromine compounds has been mainly focused [55]. The halogen content is high for self-extinguishing in polypropylene e.g. 40% chlorine or 20% bromine [56].

Bromine compounds were showed as a higher efficiency than chlorine compounds in the flame retardation [57, 58], and Noda [59] and his group obtained a patent, noting that the size of halogen minutes had a significant impact on their efficiency in inhibiting cirrhosis.

Organic and inorganic halogen compounds have been widely used for flame retardants. Most inorganic halogen compounds have been used for flame retardants in wood and paper [60]. For example, ammonium chloride (NH_4Cl) was be used as a flame retardant in polyethylene and polystyrene while ammonium bromide (NH_4Br) was used as a flame retardant with Melamine-Formaldehyde resin and styrene resin. In the study of thermal decomposition of both NH_4Cl and NH_4Br; the study was be showed that the halide (Cl and Br) is characterized at 200 C° and 250 C° respectively [61] as the solid NH_4Cl and NH_4Br minutes reduce flame energy through, In the addition, some other chlorine compounds were used as flame retardants. The Aqueous-Magnesium Chloride ($MgCl_2.6H_2O$) [62] was be used with paper and three types of chlorine compounds were used with wood [63] $AlCl_3.6H_2O$, $CaCl_2.XH_2O$, and $ZnCl_2$. In this case both of chlorine ion and the water molecule play as a role in the flame retardant mechanism [62].

Organic halogen compounds have be evolved as flame retardants for various plastics [64] such as polyethylene, polypropylene, polystyrene and high impact polystyrene. Those compounds may be used alone or in the combination with Sb_2O_3 and other synergistic agents [65]. Organic chlorine and bromine compounds are the first types of flame retardants [66]. Bromine compounds are generally more effective for chlorine compounds that depend on the compositions of these compounds. The halogen bond strength of the molecule and the ease of halogen halide release during the combustion process [67].

The aliphatic chlorine has been used as flame retardants and sold in the form of chlorinated paraffin's, which is used with low-melting polymers such as polyethylene due to limited thermal stability [68].

Many organic and inorganic phosphorus compounds are used as flame retardants in polymer composites [69]. Although their mechanism of action is less understood than the mechanism of halogenation [70], phosphorus compounds are often used synergistically with nitrogen and halogen compounds and synergistic or co-ordinated means are the use of two or more inhibitors Flame with polymeric material for the purpose of increasing the efficiency of disability [71]. However, it is not necessary that all phosphorus compounds act as flame retardants with the same degree of efficiency. Flame retardation is not a linear function relative to phosphorus content in the material used [72]. The use of phosphorus compounds Wide in vehicles high-oxygen polymers such as Cellulose and that its mechanism of work in blockage is condensing phase as it reduces the contribution of hydrocarbon fuel as well as producing a quantity of carbonaceous char in the processes of estrangement of hydroxyl groups, with poly phosphoric acid of the compounds inorganic phosphorus that have shown significant efficacy in blocking polyolifin polyphosphate that is red phosphor [73]. Red phosphorus is more efficient by increasing its concentration until it reaches the maximum and then any increase in concentration will produce adverse results [74].

Peters P. [75] noted that the 8% concentration of red phosphorus yields the best results and that any increase in concentration will reduce its efficiency in blocking the polyethylene hue. Walters & Braddy [76] noted that the low volumes of halogen compounds improve the effectiveness of red phosphorus in inhibiting the combustion of polyolefins and polyvinyl chloride. Cranzo [77] noted that red phosphorus is active in the steel phase mainly as it converts to phosphoric acid, which accumulates during combustion, forming a layer that reduces the flow of volatile gases into the flame zone and increases coal formation. Red phosphorus is also effective in phase Which turns into phosphorus Oxide, which blocks or inhibits the series of flame reactions and removes the free radicals that are the basis of the continued ignition and that the addition of small amounts of nitrogen compounds will improve the action of phosphorus in blocking the homing of polyolefins [78, 79]. Organo-phosphorus, such as phosphine and phosphates, most of which act synergistically with compounds containing nitrogen or halogen or both [80] .The effectiveness of these compounds in blocking the polymerization of polymers is more in the vapor phase than the sold phase, noting that the phosphorus is not present in the residue of polycarbonate combustion products olefins and polystyrene [81, 82]. Rosser [83] have proposed the mechanism of action of triphenyl phosphine compounds Ph_3P and triphosphonal phosphine oxide Ph_3PO, and many research [84, 85, 86, 87] on the effectiveness of phosphorus compounds in vapor phase.

Antimony compounds are rarely used to inhibit polymerization because of their low efficiency. He noticed, Martin [88], effectiveness of low-lying triphenyl antimony Ph_3Sb in the flame inhibition of epoxy resin when used alone and interpreted on the basis of oxidation and composition of antimony oxide that appears clear in the effectiveness of inflammability disability. Also, the majority of antimony organic compounds with aqueous stability and a few expensive price and low efficiency. in the other hand, antimony oxides, antimony tri-oxide Sb_2O_3 and antimony pentoxide Sb_2O_5 low efficiency and high efficiency appear in the flame inhibition of polymeric materials [89].

The antimony efficient compounds have shown high flame retardant of polymeric materials when used jointly or synergistically with various halogenated compounds, and use spread widely and commercially. The most commonly used antimony compounds are antimony trioxide [90]. Studies [89-91] have shown that the efficiency of halogen compounds with antimony trioxide as follows:

Aliphatic compounds > Cyclic compounds > Aromatics

The bromine compounds with the antimony trioxide are more widely used and widespread than chlorine compounds because they are cheaper, more stable and more efficient than chlorine compounds [92, 93].

The agroup of researchers [94-96], were prepared a group of organic compounds, halogenated type mixed haloantimonates (III) (aliphatic or aromatic) element containing antimony in the form of synthetic on elemental bromine and chlorine, and the ratio between the antimony to halogen (1:3), which represents the optimal ratio to give the best efficiency in the flame retardation and prevent the combustion of various polymeric materials and these compounds are: $Et_4N\ [C_2H_5SbBr_2Cl]$, $Et_4N\ [C_6H_5SbCl_2Br]$, $Et_4N\ [C_6H_5SbBr_2Cl]$ and $Et_4N\ [C_6H_5SbCl_2Br]$ and through the tests conducted for these compounds with materials different polymer including high and low density polyethylene, poly propylene and polystyrene. Those compounds were showed high efficiency for flame inhibition and prevent the combustion of polymeric materials, as well as the study of the act synergistically oxide of aluminum with chlorinated paraffin for ignition polyethylene and high density of polypropylene showed high efficiency [97].

The boron compounds although the effect of boric acid and boron salts have long been inhibited for the polymerization of polymers. They have remained less widely used than other flame retardants. The most important boron compounds are widely used for boric acid and borax, polymer [95]. The various boron compounds act synergistically with halogens and work in the steam phase by forming boron triglycerides [96].

1.4.5 Flame – Retardant in Polyester and Epoxy Resins

Due to the wide and multiple uses of unsaturated polyester resins and epoxy resins in various areas of life, so many chemical compounds have been used to inhibit its combustion, such as various halogen compounds as bromine and chlorine compounds [98]. Halogen compounds may be used alone or through synergistic action with other substances such as antimony, and phosphorus compounds alone or through synergistic action with nitrogen compounds, halogen compounds, or both. In general, the thermal stability of polyester and epoxy resins can be increased by increasing aromaticty or cyclic (ring structure) in the resin chain [99, 100].

Fire-resistant of epoxy resin can also be obtained in a number of ways, including the use of halogen elements, which are incorporated as an essential part of epoxy resin synthesis, mainly chlorine and bromine, through the use of raw materials containing these elements in the preparation of epoxy resin such as (tetra chloro-bisphenol A or tetra bromo-bisphenol A) and therefore have an epoxy resistant to flammability and self-extinguishing [101].

1.5 Aim of this Research

This work aims to prepare a group of heterocyclic compounds and measurement of their effectiveness as flame retardants for polyester and epoxy resins are to obtain new polymers that are highly efficient in flame resistance by adding limited percentages of additives to heterocyclic organic compounds to unsaturated polyester and epoxy resins .

The tests which are used to measure the effective of flame retardant materials are:

1- Limiting oxygen index (LOI).
2- Rate of burning (R.B.).

CHAPTER TWO

Experimental

2. Experimental Part

2.1 All those Chemicals

All chemicals used were produced by companies. (Sigma),(Fluka),(G.C.C),(KSA),(HIMEDIA),(BDH) and (MERCK); Table (2-1), shows all chemicals were used in this work.

Table (2-1): All those chemicals and their supplier

No.	Chemical Material	Formula	Purity %	Company
1	Acetyl acetone	$C_5H_8O_2$	99.0	HIMEDIA
2	Thiosemicarbazide	CH_5N_3S	99.0	Fluka
3	Thioacetamide	C_2H_5NS	98.0	B.D.H
4	Cysteine	$C_3H_7NO_2S$	95.5	B.D.H
5	Sodium nitrite	$NaNO_2$	98.0	B.D.H
6	Hydrochloric acid	HCl	99.0	B.D.H
7	Thiourea	CH_4N_2S	95.5	B.D.H
8	Benzil	$C_{14}H_{10}O_2$	98.0	Fluka
9	Sodium hydroxide	$NaOH$	98.0	B.D.H
10	Absolute Alcohol	C_2H_5OH	99.8	B.D.H
11	Sulphuric acid	H_2SO_4	99.0	B.D.H
12	Acetone	C_3H_6O	99.9	G.C.C
13	Potassium chloride	KCL	99.6	B.D.H
14	Unsaturated polyester resin , hardener type (MEKP)	-	-	Indu. Chem. and Resins Co. Ltd (KSA)

15	Epoxy resin , type (CY223) , hardener type (HY956)	-	-	Ciba-Geigy Co . (Swiss)
16	Diethyl terephthalate	$C_{12}H_{14}O_4$	99.0	SIGMN
17	Sulfobenzoic anhydride	$C_7H_3O_4S$	95.0	SIGMN

2.2 Instrument Analysis and Equipment:

1. Infrared spectrophotometer, Fourier Transformer Infra-Red Spectroscopy. The FT-IR spectra in range 500-4000 cm^{-1} were obtained by using potassium bromide disc on FT-IR – instrument model (8400 s) Shimadzu spectrophotometer/Japan. Kufa University

2. **The Proton Nuclear Magnetic Resonance**, ^{1}H-NMR-Bruker spectrometer, 300 MHz, Switzerland, France with DMSO d$^{\mathbf{6}}$, Canada/ Kashan University, Iran.

3. **The Carbon Nuclear of Magnetic Resonance**, ^{13}C-NMR - Bruker spectrometer, 300 MHz, Switzerland, Canada/ Kashan University, Iran.

4. **Elemental analysis,** Micro analytical unit, 1108 CHNS Elemental analyzer. , Kashan University, Iran.

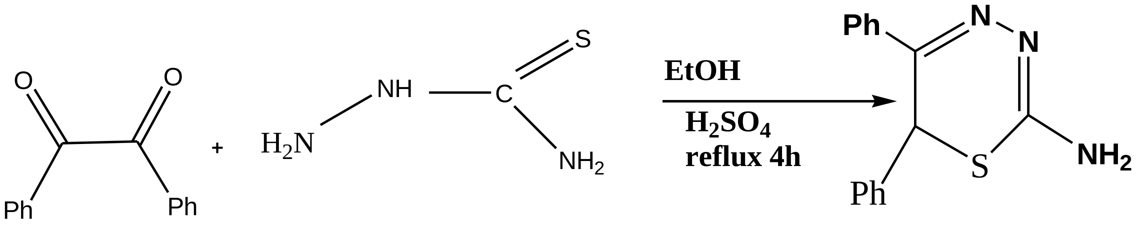
5. **Thin layer chromatography (TLC)** was carried out by using alumina plates percolated with silica-gel, compound was detected by Iodine vapor.

2.3 Synthesis of additives

2.3.1 Synthesis of additive (A1) [102]

(5,6-diphenyl-6H-1,3,4-thiadiazin-2-amine)

Prepare was the mixture by dissolving (2g , 10mmole) of benzil into 100 mL of absolute ethanol with continuous stirring and then added (0.6 g, 6.6mmole) of thiosemcarbized and then added 5 mL of concentrate sulfuric acid. The mixture was heated to the ($78C^0$) under reflux for 6h. After cooling to room temperature, the precipitate was filtered and was refluxed with absolute ethanol and weight. As the following equation.

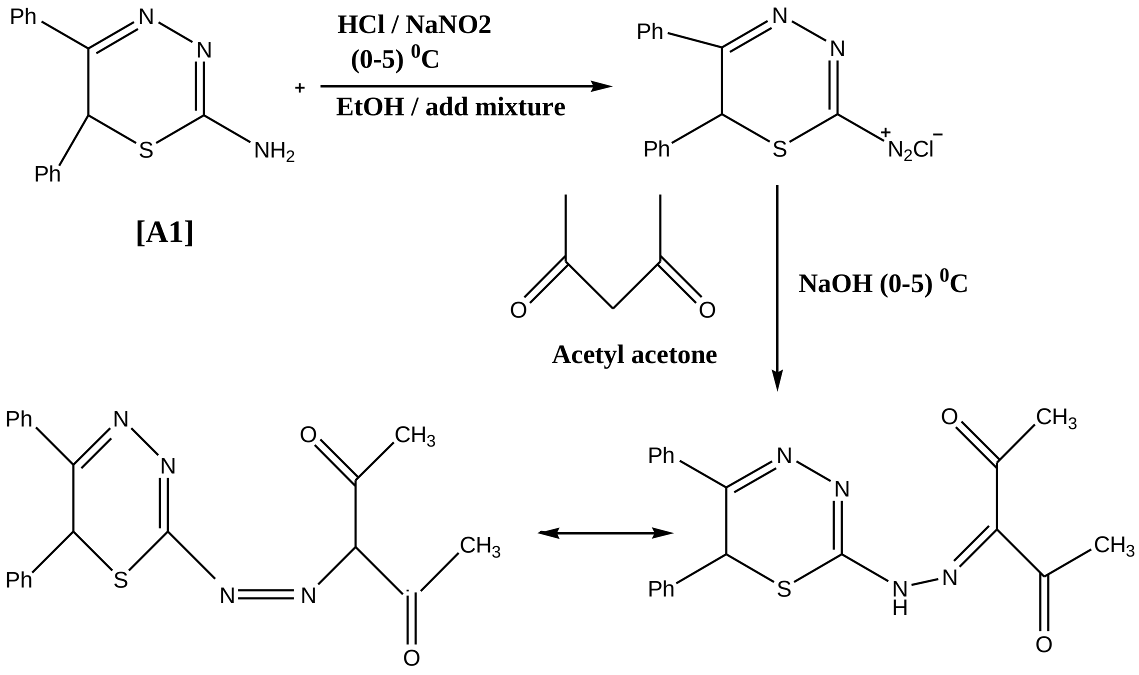


[A1]

2.3.2 Synthesis of additive (A2) [103]

(Pentane -2,3,4-trione3-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl) hydrazine])

Prepared was the mixture by dissolving (2.67g,10mmol) of the compound (A1) in 5 ml of concentrated hydrochloric acid and (10 mL) of distilled water .The mixture was be cooled at (0-5C˚) and added (0.7gm,10mmole) of sodium nitrite ($NaNO_2$) dissolve in 10 ml of D.W with continuous stirring .Leave the solution to settle for 15 minutes. Then added the diazonium solution formed with continuous stirring to a solution of (0.88g,10mmole) of (Acetyl acetone) dissolving in 50mL of absolute ethanol and 10 mL of sodium hydroxide 10% . The solution is colored in the light orange and the precipitate was formed .the left to the following day and a precipitate formed that was filtered and recrystallized from absolute ethanol, as the following equation .



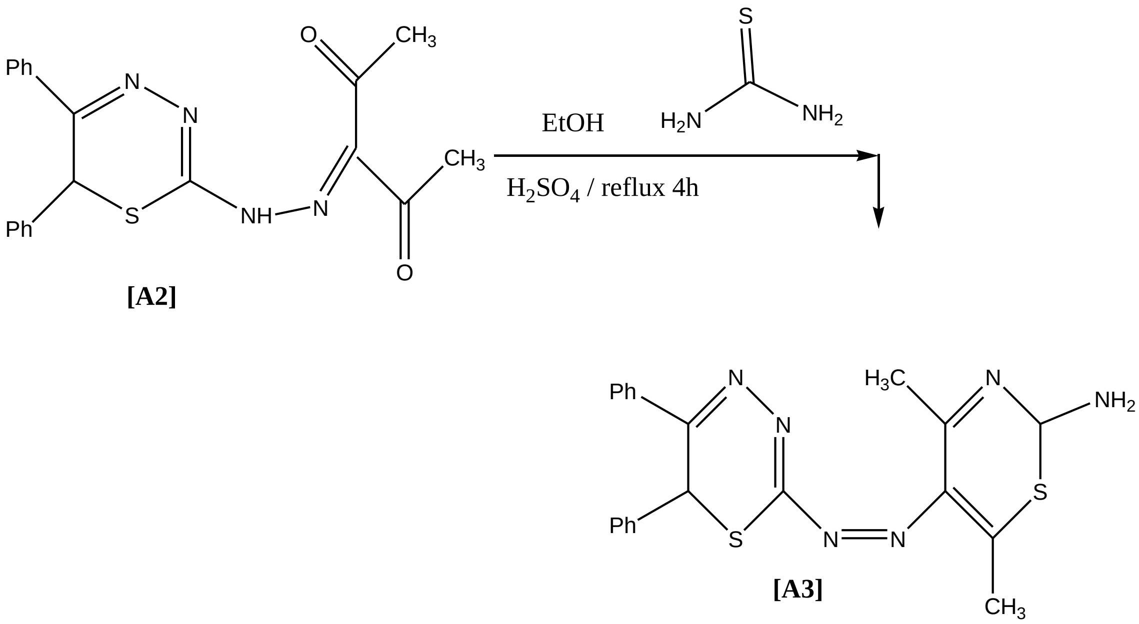
[A1]

[A2]

2.3.3 Synthesis of additive (A3) [104]

(5-[(z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-4,6dimethyl-2H-1,3-thiazin-2-amine)

A mixture of compound (A2) (0.42g, 1mmol), absolute ethanol (50mL), Thiourea (0.07612g, 1mmol) with continuous stirred and was added 5mL of concentrate sulfuric acid, the mixture was reflux for 4h under 78C° .The mixture was be cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol, as the following equation .



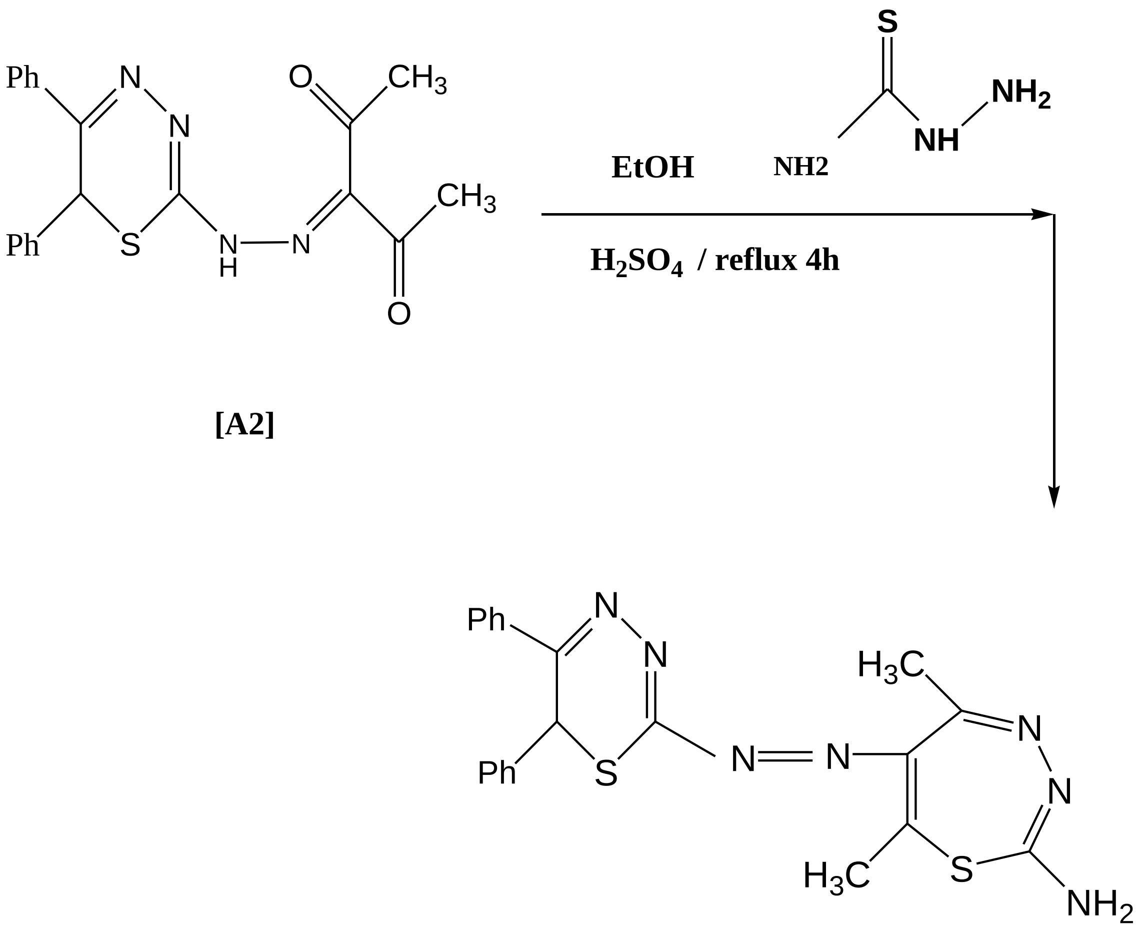
[A2]

[A3]

2.3.4 Synthesis of additive (A4)[104]

(6-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-5,7dimethyl-1,3,4-thiadiazepin-2-amine)

The compound (A2) mixture (0.42g, 1mmol) , absolute ethanol (50ml) , thiosemicarbized (0.09114g , 1mmol) with continuous stirred and was added (5ml) of concentrate sulfuric acid, the mixture was reflux for 4h under 78C° . The mixture was be cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol ,the percentage of yield was (80%) , as the following equation .



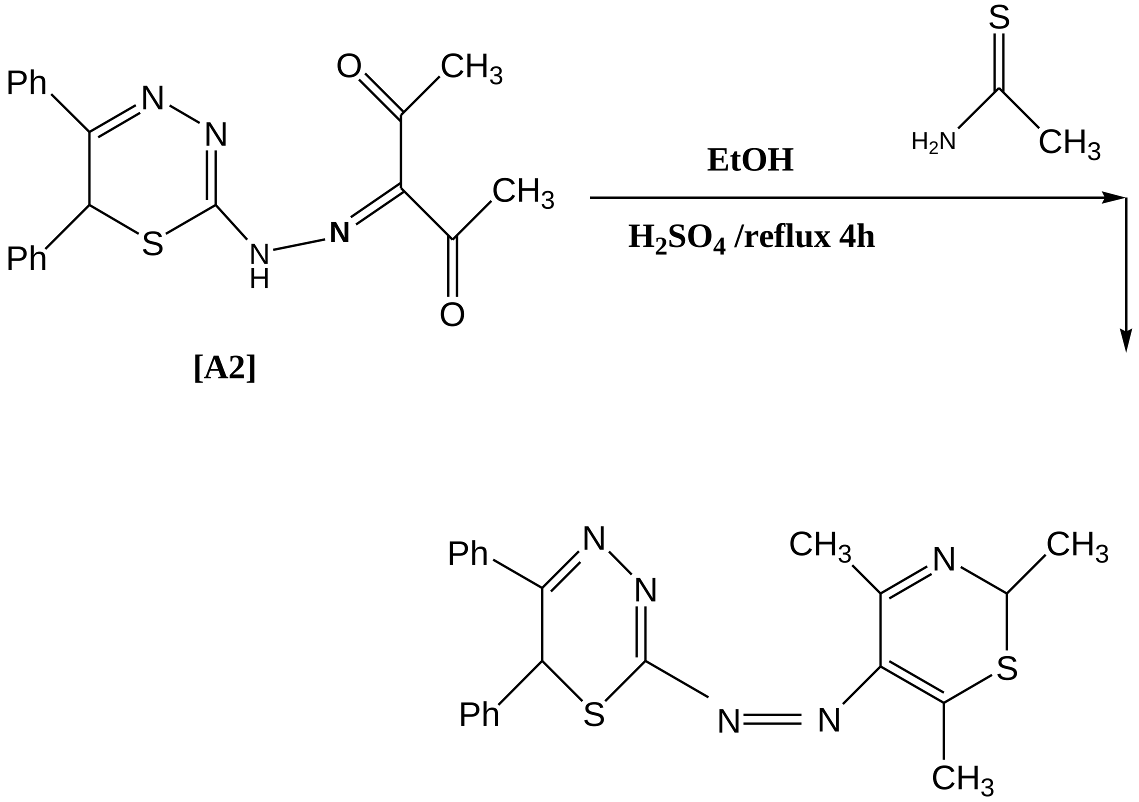
[A2]

[A4]

2.3.5 Synthesis of additive (A5)[104]

(5,6-diphenyl-2-[(Z)-(2,4,6-trimethyl-2H-1,3-thiazin-5-yl)diazenyl]-6H-1,3,4-thiadiazine)

A mixture of compound(A2) (0.42g,1mmol) and Thioacetamide(0.07513g,1mmole) dissolve in absolute ethanol (50mL), with continuous stirred and added (5mL) of concentrate sulfuric acid , the mixture reflexed for 4h under 78C° , the mixture cooled in the ice bath and a precipitate formed that filtered and recrystallized from absolute ethanol, as the following equation .



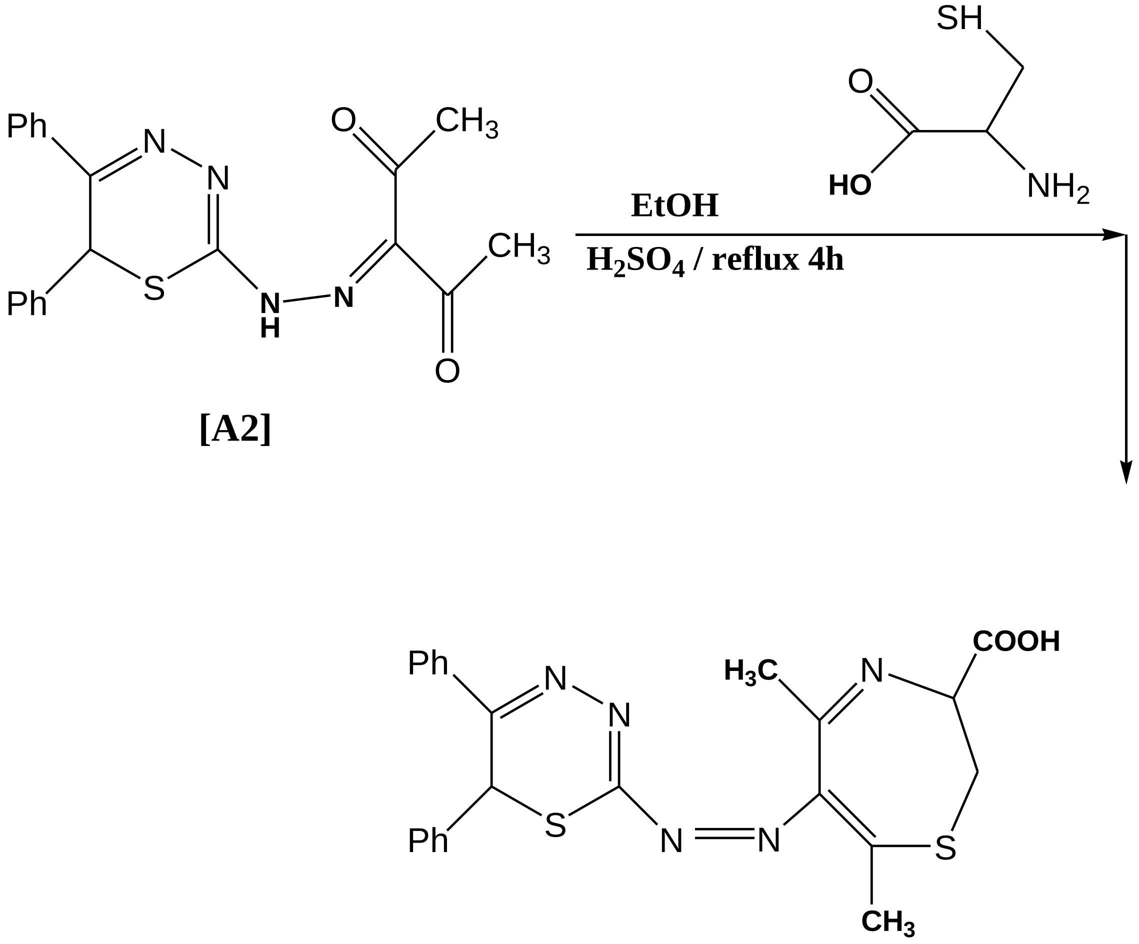
[A2]

[A5]

2.3.6 Synthesis of additive (A6) [105]

((4Z,6E)-6-((Z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl)-5,7-dimethyl-2,3-dihydro-1,4-thiazepine -3-carboxylic acid)

A solution of compound (A2) (0.42g , 1mmol) , absolute ethanol (50mL) , Cysteine(0.121g , 1mmol) with continuous stirred and was added (5mL) of concentrate sulfuric acid , the mixture was reflux for 4h under $78C^o$, the mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol, as the following equation .



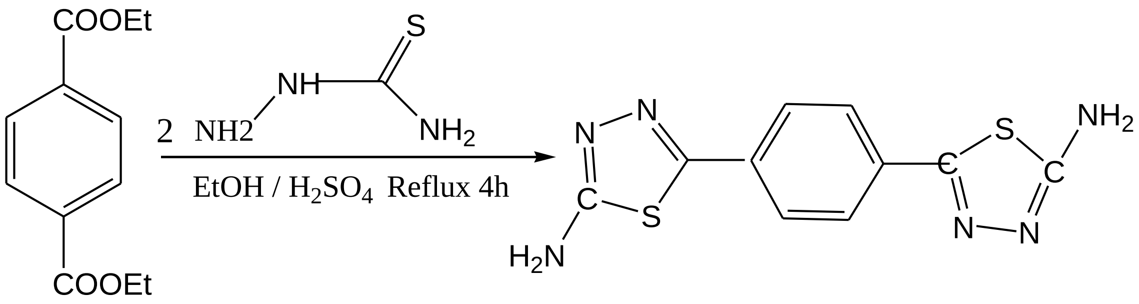
[A2]

[A6]

2.3.7 Synthesis of additive (A7) [106]

(5-(1,4-phenylene)bis (1,3,4-thiadiazinol-2-amine))

A mixture of Diethylterephthalate (0.222g , 1mmol), absolute ethanol (100mL) , Thiosemicarbized(0.1822g , 2mmol),with continuous stirred and was added (5mL) of concentrate sulfuric acid , the mixture was refluxed for 4h under 78C° , the mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol, as the following equation .

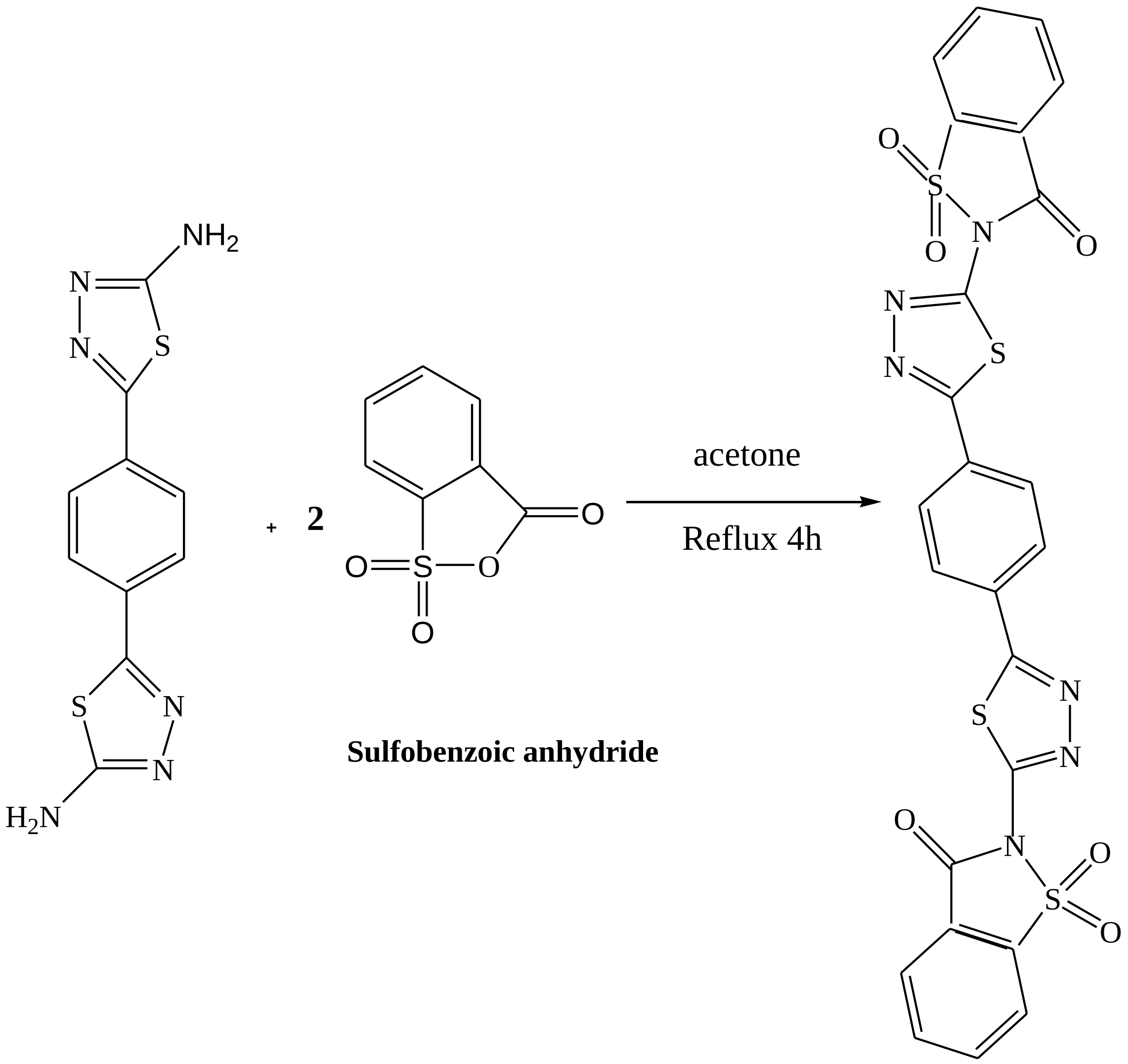


[A7]

2.3.8 Synthesis of additive (A8) [107]

(2,2-(1,4-phenylene-bis-(1,3,4-thiadiazole)-5yl)bis(1,2-benzisothiazol-3(2H)-one) 1,1,1,1,-tetraoxide)

The compound mixture (A7) (0.222g , 1mmol) ,acetone(100mL) with continuous stirred and was add (0.368g , 2mmol) of sulfobenzoic anhydride ,the mixture was reflexed for 4h under 56C°, the mixture was be cooled in the ice bath and a precipitate formed that was that was filtered and recrystallized from absolute ethanol , as the following equation .



Sulfobenzoic anhydride

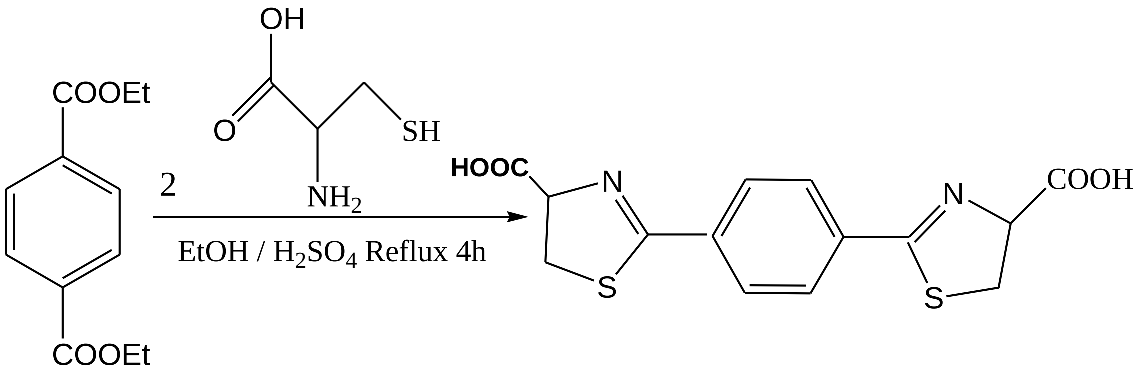
[A7]

[A8]

2.3.9 Synthesis of additive (A9)[106]

(2,2-(1,4-phenylene)bis(4,5-dihydro-1,thiazole-4-carboxylic acid)

A mixture of Diethyl terephthalate (0.222g , 1mmol) ,absolute ethanol(100mL),C ysteine(0.242g , 2mmol) with continuous stirred and was be added (5mL) of concentrate sulfuric acid , the mixture was refluxed for 4h under 78C° , the mixture was be cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol , as the following equation .

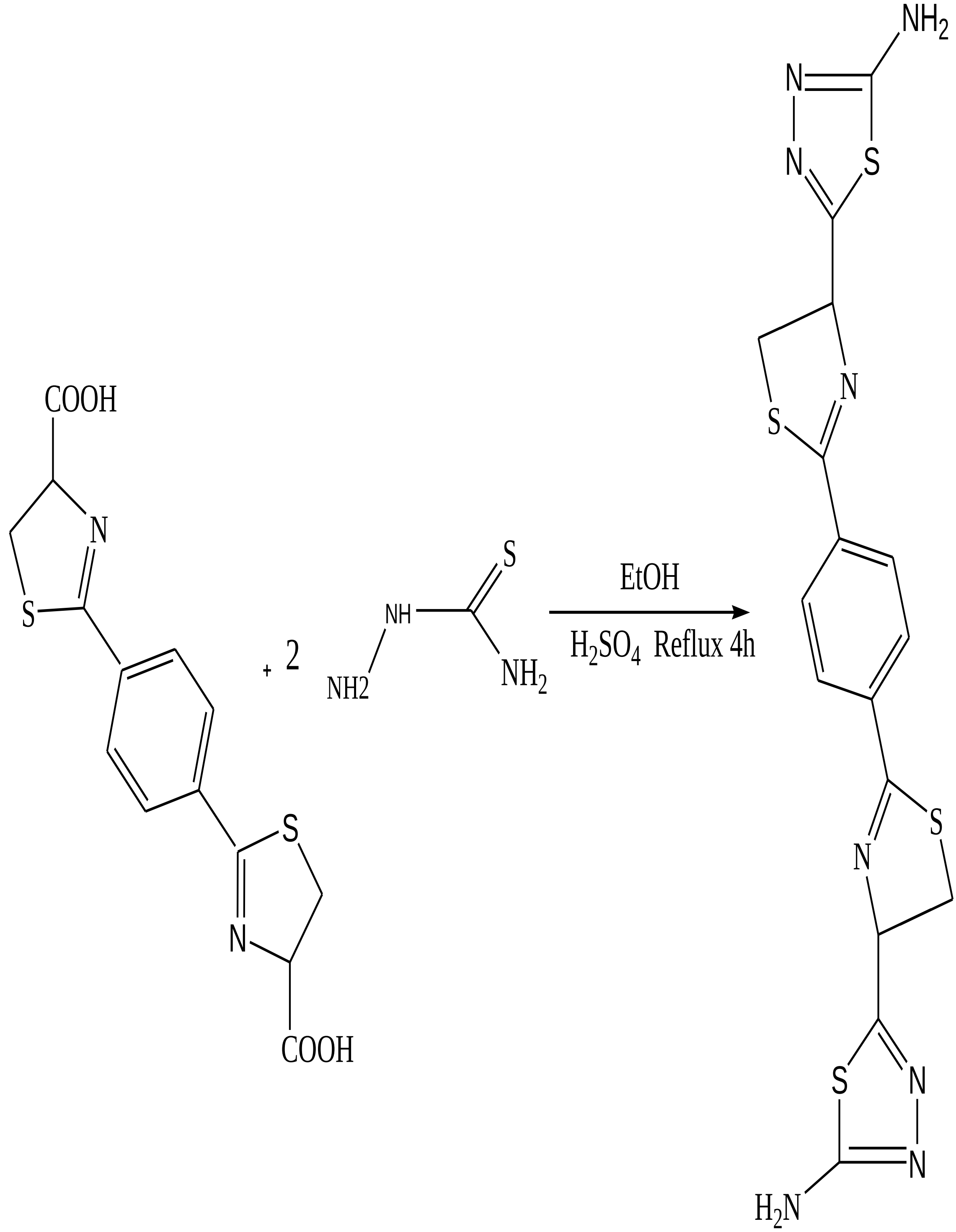


[A9]

2.3.10 Synthesis of additive (A10) [108]

(5,5̀-[1,4-phenylene bis(4,5-dihydro-1.3-thiazole-2,4-diyl) bis (1,3,4-thiadiazol-2-amine))

The compound mixture (A9) (0.42g, 1mmol), absolute ethanol (50mL), Thiosemicarbazide (0.18 g , 2mmol) with continuous stirred and was add (5ml)of concentrate sulfuric acid ,the mixture was refluxed for 4h under 78C^{o} , the mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol , as the following equation .


COOH
N
S
+ 2
NH
S
NH2
NH$_2$
EtOH
H$_2$SO$_4$ Reflux 4h
NH$_2$
N
N
S
N
S
S
N
S
N
N
H$_2$N
COOH

[A9]

[A10]

Table(2-2):Melting point, Molecular weight, Yield percentages and R_f for the synthesis compounds.

compound	M.WT	M.P(+2)	R_f	Yield%
A1	267	189	0.8	82%
A2	378	182	0.8	84%
A3	420	124	0.8	79%
A4	433	174	0.9	80%
A5	419	168	0.9	82%
A6	463	170	0.8	80%
A7	276	175	0.7	80%
A8	608	157	0.9	78%
A9	336	155	0.8	82%
A10	446	170	0.6	79%

2.4 Flame Retardants Tests

The two standard methods [Limiting oxygen index (LOI) and Rate of burning (R.B.)], were used to measure the effect of the additives as flame retardants, as in below:

2.4.1 Limiting Oxygen Index (LOI) by using (ASTM: D-2863)

This method was one of the most widely used laboratory methods in determining the flammability of different polymer materials. This is achieved by the measuring of minimum concentration of oxygen gas (expressed as a percentage to the volume of oxygen gas), and the continued ignition of polymeric material flowing through a mixture of oxygen and nitrogen to the test tube [109, 110] .

The Limiting Oxygen Index (LOI) is measured by a balance or stability is achieved by the amount of the heat generated and the combustion process of the amount of heat lost to the environment [111]. To do, the time period for combustion is determined or the height of the burning part is determined within a specified period of time. By taking the above factor into account, the amount of oxygen gas the crisis caused by the combustion during that period of time or at a certain distance is called the Oxygen Index (OI) [110]. This method of examination includes the following:

2.4.1.1 Preparation of test samples

Three sample were taken for each model and prepared the samples were length (130±5) mm, width (6.5±0.5)mm and thickness(3.0±0.1)mm.

2.4.1.2 Equipment and Tools

All laboratory devices used in the department of physics / college of sciences/ university of Baghdad, were manufactured to achieve the measurement required for the method of examination (ASTM:D-2863) as in figure(2-1). The device components as shown:

1- Glass tube

A glass tube resistant to internal diameter(75mm) and length (450mm), bottom base based on the pedestal stand enclosed in Aluminum foil, contain a hole at the height of (80- 100 mm) of the bottom base attached to a rubber tube in the form of a letter T and diameter of (3-5 mm) for the purpose of entering the mixture of gasses and equipped with a metal clamp at an appropriate height for the purpose maintain clean base of the tube as figure (2-1).

2- Specimens holder

It is a metal frame with a dimensional of (37.5 × 100) mm in which the model sliders on to a metal rod based on the base of the metal holder

3- Flow meter

Two types of flow meters were used; The first type is of the type FM112- 02 ST , The other type and each device is divided from 10 to 150 Mm .The maximum flow velocity in the laboratory condition 832m1/min for the first flow and 4077m1/min for the second flow .

4- Pressure Gage Regulator:

For this purpose, one is used for nitrogen gas and the other for oxygen gas.

5- Ignition Source:

The use of a (3mm) diameter thermal torch works with natural gas. The flame of blue flame was arranged from, the torch length (5-25)mm.

6- Gases Source:

A cylinder of oxygen gas and cylinder of nitrogen gas were used by AL-Mansour plant and was purity 99.99%

7- Timer.

2.4.1.3 The method of work

1- The gas flow meters were balanced by connecting the two flow meters in a continuous manner and then passing the nitrogen and oxygen gas through which the gas flow velocity was regulated to be equal in both. It is advisable to perform this balancing process continuously.

2- The sample was placed vertically within the special catcher as shown in figure (2-1) and the top end of the model was at least 100mm form the top of the open glass cylinder from the outside.

3- The flow velocity of nitrogen gas was maintained with a concentration of 82% during the selection process, a velocity of volume of oxygen gas at a concentration of 18% for flammable samples and 24% for non-flammable samples.

4- Mixture of gases in the flow can be heard inside the glass column for 30 sec., before starting the ignition.

5- Regulate the flame of the torch so that its length ranged between (10-25) mm.

6- The sample ignites by inserting the thermal torch into the glass column (test tube) so that the blue flame touches the top of the head of the sample and the flame continues to ignite until the sample ignites and then ignites the torch and begins to calculate the time.

7- If the amount oxygen concentration through the oxygen – nitrogen mixture is sufficient to burn 50mm of the sample before self-extinguishing or continued combustion for at least three minutes. The concentration of oxygen and the concentration of nitrogen in the mix are recorded.

8- If a self-extinguishing occurs before reaching the measurement referred to in paragraph (7), the oxygen volume increased and in this case the sample is replaced.

9- The steps are returned from (1-8) until the best reading is achieved , which is the minimum concentration of oxygen gas required to continue the ignition of 50 mm of the sample or to continue ignition for at least three minutes before self-extinguishing.

D- Calculation

The Limiting Oxygen Index (LOI) is required to complete test and can be calculated by the equation [112]:

$$n\% = \frac{O2\%}{O2\% + N2\%} \times 100\%$$

n = (LOI) Limiting Oxygen Index

O_2= Flow velocity of oxygen gas mL/sec

N_2= Flow velocity of nitrogen gas mL/sec

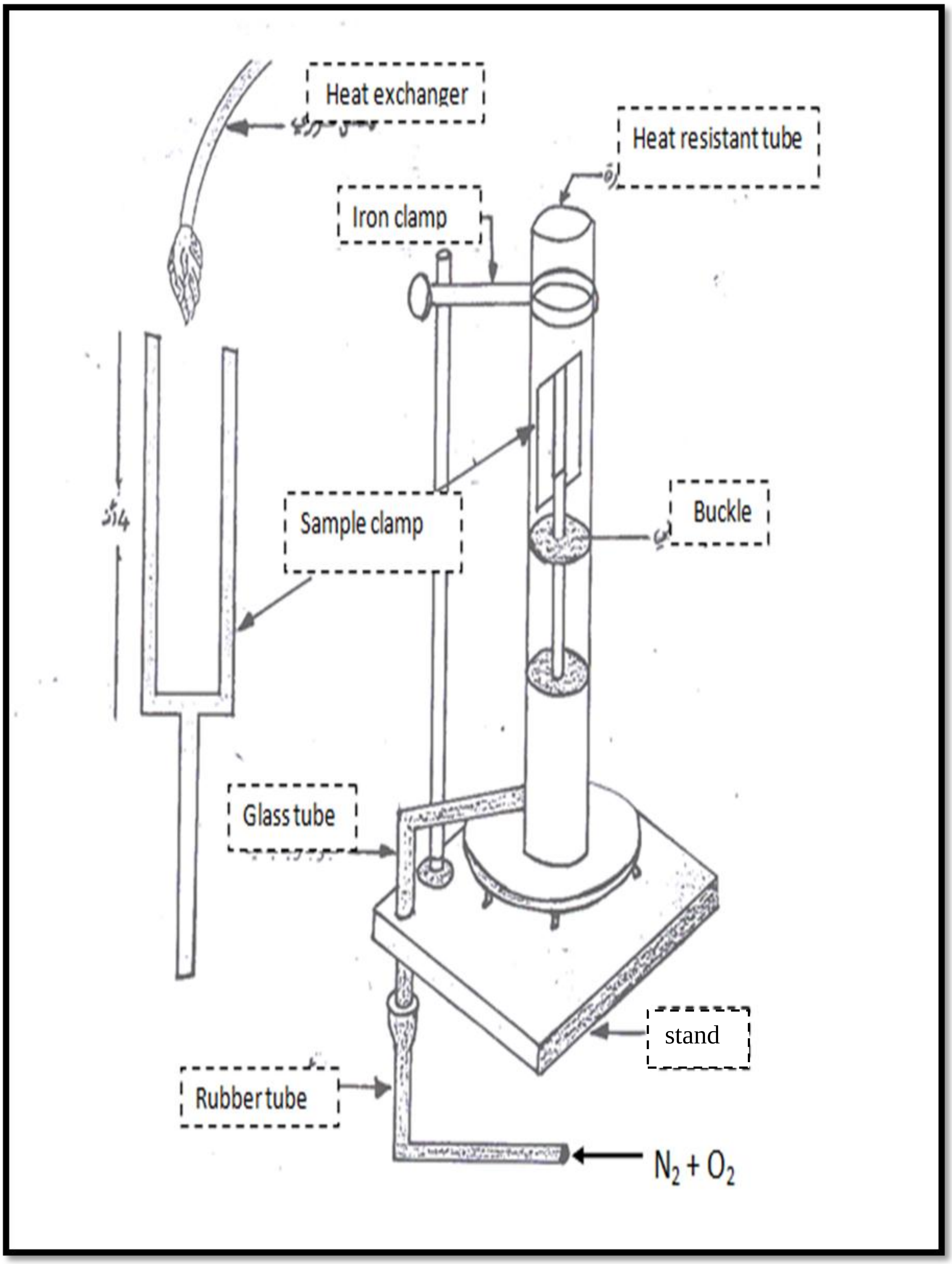


Figure (2-1): Limiting Oxygen Index (LOI)

2.4.2 The Rate of burning (R.B.), The Average time of burning (ATB), The Average extent of burning (AEB), The Self-Extinguishing (SE) and The Non- Burning (N.B.), were measurements by using (ASTM:D-635):

This method was one of the most widely used laboratory methods to measure the speed of flame spread in various polymer materials, calculate the time period of the burning process, and calculate the rate of burning distance of the model during that time period [113].

They are widely used in polymers that can be converted into sheets or rods. Through this method, the probability of self-extinguishing can be determined after a period of time or the combustion of the whole model. Polymers that can be tested in this method are classified as combustible, non-combustible and self-extinguishing after a period of combustion [114]. This method of examination includes the following:

2.4.2.1 Preparation of test samples

At least three samples were selected for each model and each sample was length wise (125 ± 5) mm and width (130 ± 125) mm and thickness (3.0) mm and made the edges of the sample smooth after the cutting process.

2.4.2.2 Place of examination

All laboratory devices were used in the department of physics / college of sciences/university of Baghdad, were manufactured to achieve the measurement required for the method of examination (ASTM:D-2863) as in figure(2-2).

2.4.2.3 The method of Test

1. Install the sample horizontally on the metal clamp as shown in the figure (2-2).

2 - Regulation of the gas burner to get a blue flame height of about 25 mm.

3. The sample edge is exposed to the flame of the lamp for 30 seconds or until the flame reaches the edge of 25 mm from the edge of the sample. This time is the exposure time (T_0)

4. The starting by recording the time required for the first drop of the polymeric material.

5. The time required to burn 100 mm in length from the model or when self-extinguishing is recorded in the burning model (T).

6. The length of the unburned part (residual) of the model shall be measured when self-extinguishing (X) is achieved.

7. The length of the welded part of the model shall be measured when self-extinguishing occurs.

8. The processes shall be returned from (1-7) of the three samples for each model.

2.4.2.4 Calculated the method of examination (ASTM: D-635)[115]

1. Average time of burning (ATB)

$$ATB = \frac{No.of\ samples}{\sum(t-30)}$$

2. Average extent of burning (AEB)

$$AEB = \frac{100 - X}{No.\ \text{of samples}}$$

X= The length of the unburned part of the model

3. Rate of burning (R.B.) [cm / Min].

$$R.B = \frac{X}{t}$$

X= Length of the sample (in cm) that completely burn in time

T= Time

4. Probability of Self-Extinguishing (SE)

5 - Do not continue flammability in the sample after the removal of the thermal source, Non Burning (NB).

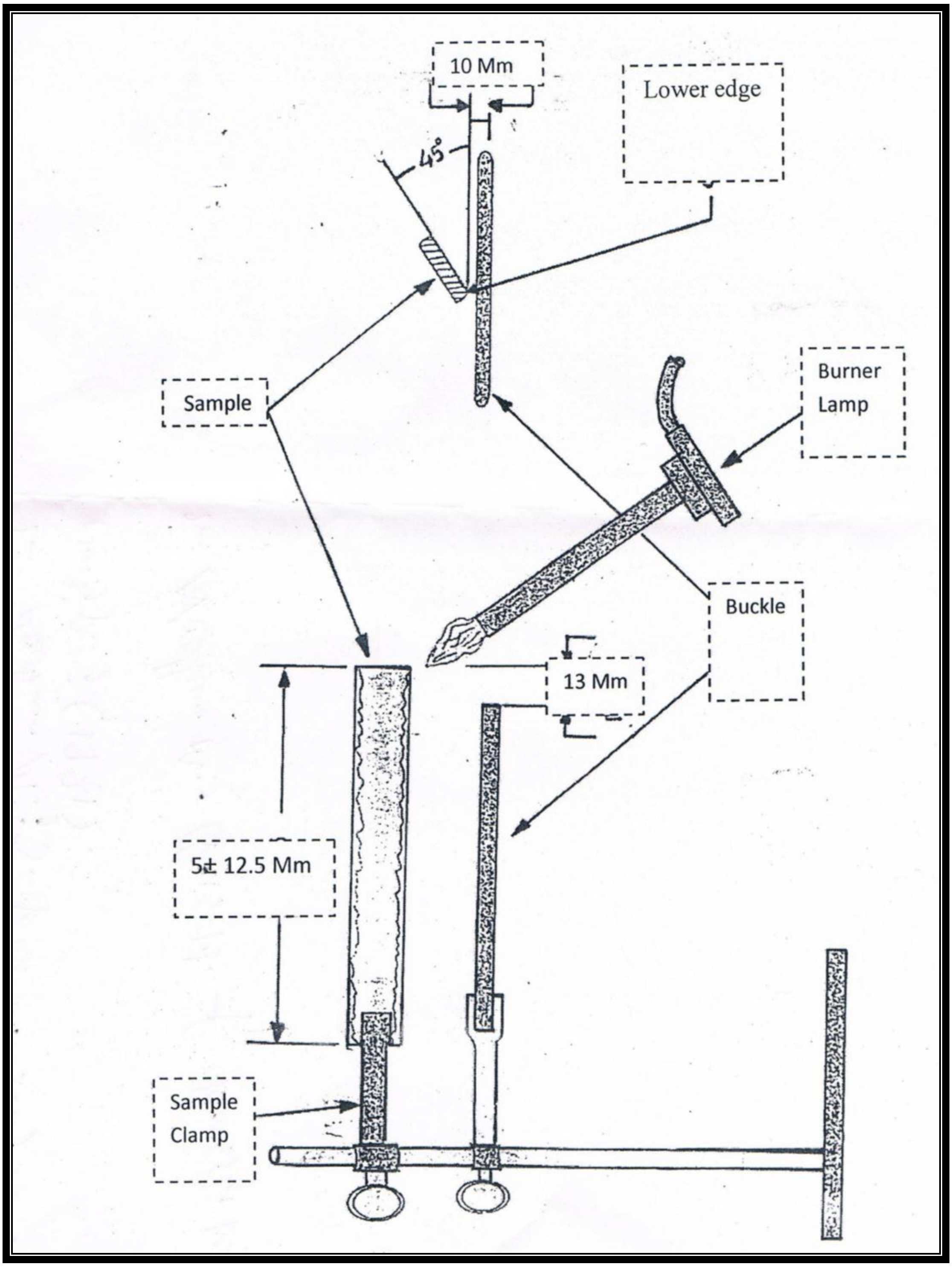


Figure (2-2): Rate of burning Instrument.

CHAPTER THREE

Results
&
Discussion

3. RESULTS & DISSCUSON

3.1 Introduction

The heterocyclic compounds are major class of organic compounds contain at least two different types of atoms in the ring such as (N, O, S, P, Se, Si, Bi and As), the presence of hetero atom gives the heterocyclic compounds many significant physical and chemical properties [116].

A large number of the heterocyclic compounds are essential to life. Various compounds such as alkaloids, antibiotics, essential amino acids, vitamins, hemoglobin, hormones and large number of synthetic drugs and dyes contain heterocyclic ring systems [117,118].

3.2 Synthesis of additives

3.2.1 Synthesis of compound (A1)

The FT-IR spectrum [119], figure(3-1) show appearance of primary amine groups (NH_2) at 3254 cm^{-1} and 3290 cm^{-1} ,appearance imine group C=N aromatic at 1620 cm^{-1}, C-S at 707 cm^{-1} ,C-H aromatic at 3043 cm^{-1}.

The ^{1}H-NMR spectrum[120] of compound (A1) show appearance of peaks (4.26) of NH_2 and (7.07 -7.88δ) of phenyl ring protons, figure(3-2)

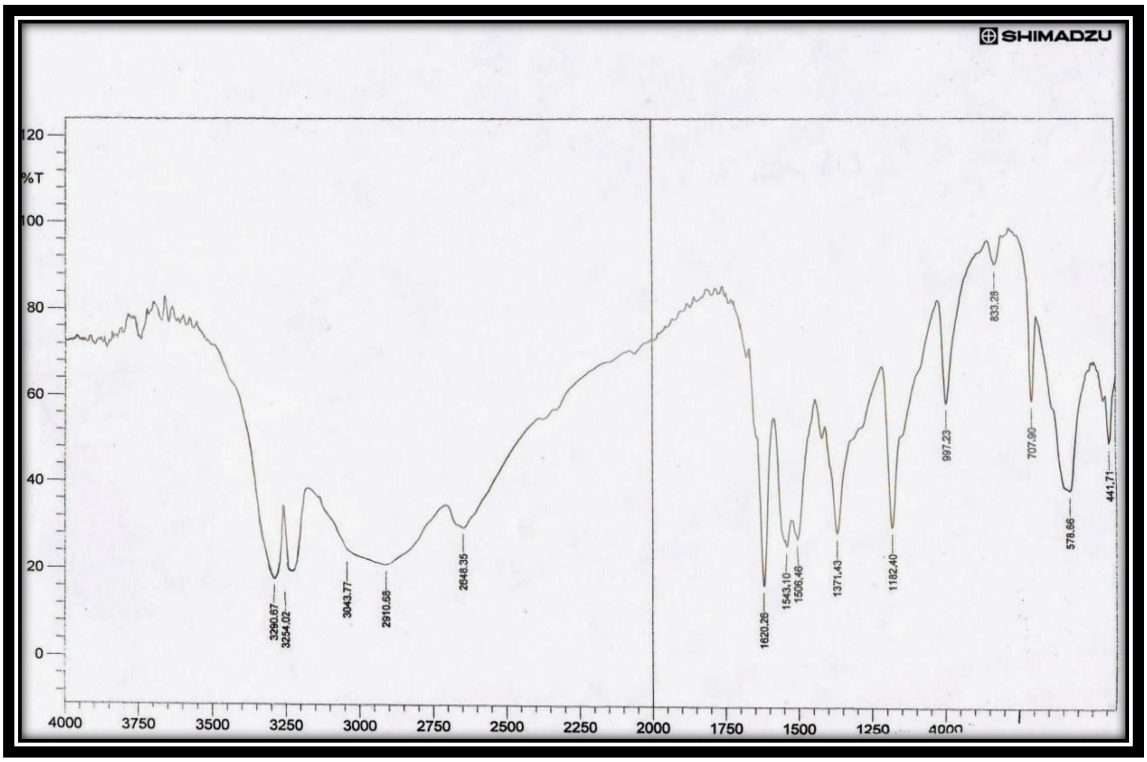


Figure (3-1) FT-IR spectrum of compound (A1)

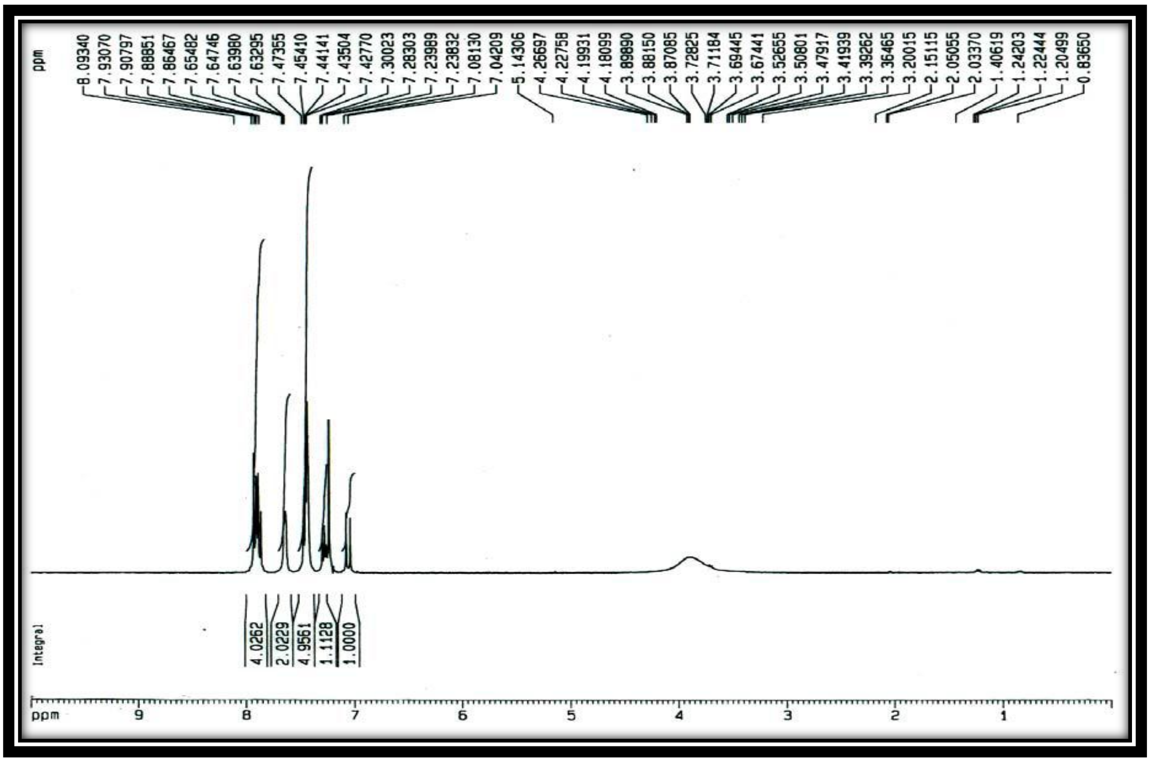


Figure (3-2): ^{1}H-NMR spectrum of compound (A1)

3.1.2 Synthesis of compound (A2)

The FT-IR spectrum of compound (A2), figure(3-3) was showing disappearance of primary amine group (NH) peaks at 3423cm^{-1}, appearance C=N at 1599cm^{-1} , C-S at 799cm^{-1}, C-H aliphatic at 2931cm^{-1} , C-H aromatic at 3095cm^{-1}, C=N aromatic ring out at 1647cm^{-1}, C=O of ketone group at 1701cm^{-1}. The ^{1}H-NMR spectrum of compound (A2), figure (3-4) protons appearance at 6.378δ of NH-H protons, 5.78δ of thiadiazin ring proton, (2.39, 3.233)δ, of $(CH_3C{=}O)_2$ dimethyl ketone groups, (7.22–7.23)δ of phenyl ring proton .

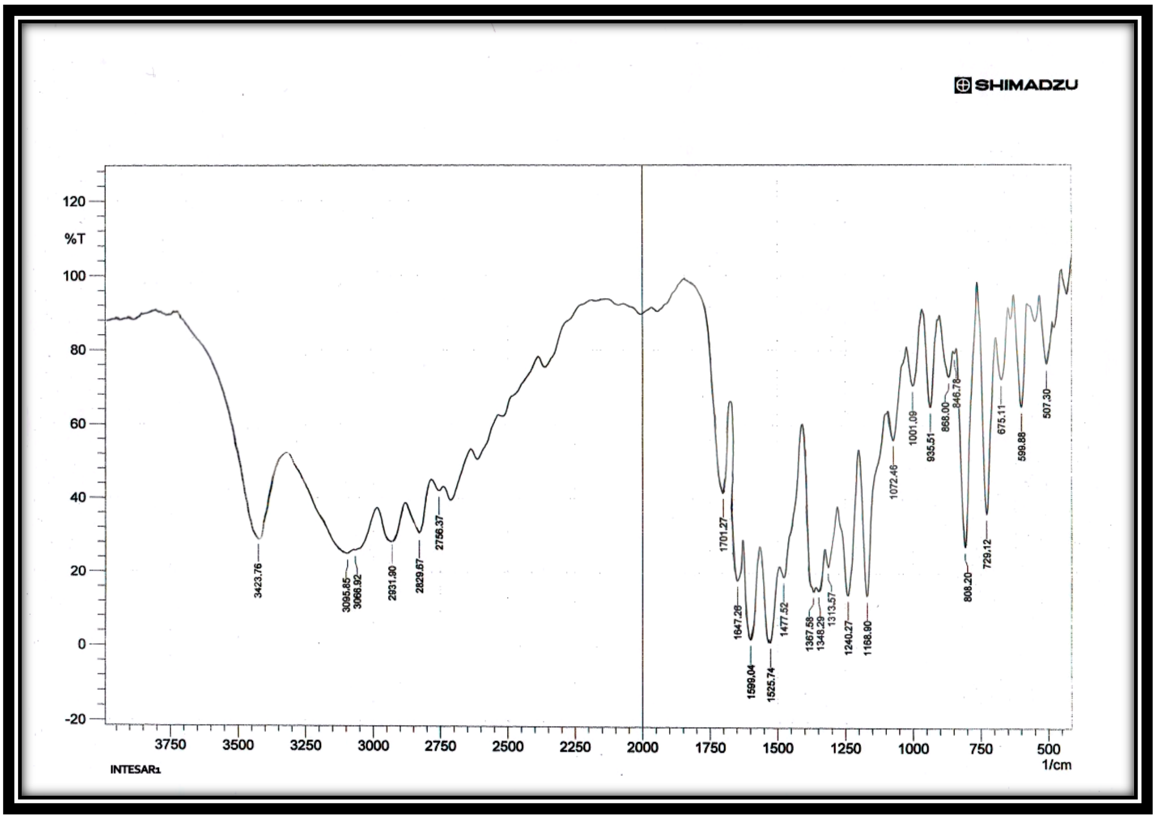


Figure (3-3): FT-IR spectrum of compound (A2)

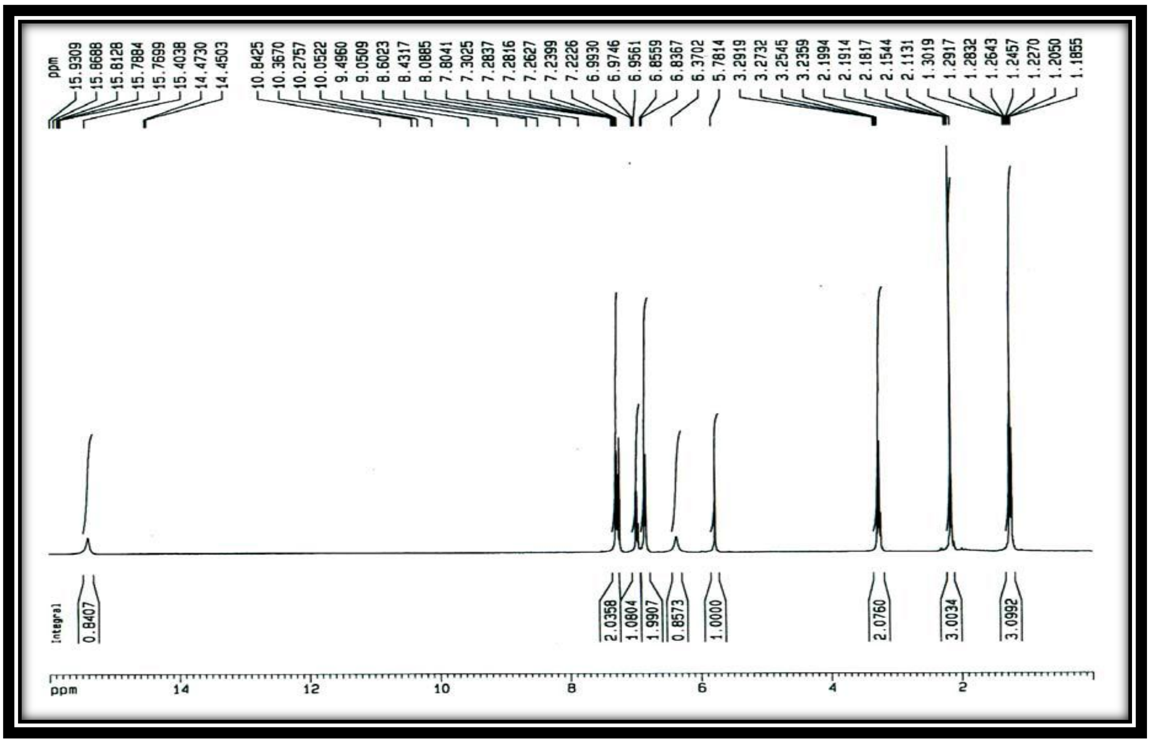


Figure (3-4): ^{1}H-NMR of compound (A2)

3.1.3 Synthesis of compounds (A3)

The FT-IR spectrum of compound (A3), figure (3-5) was showing disappearance of –N=N- azo group at (1446–1494)cm^{-1}, shows C=N of inter ring at (1600 –1647)cm^{-1}, C-H aromatic at (3022–3064)cm^{-1}, C-H aliphatic at (2922–2989)cm^{-1}, C-S peaks at (784, 824) cm^{-1} , NH_2 of primary amine group at(3281-3354) cm^{-1}.

The H^1-NMR spectrum of compound (A3), shows the appearance of phenyl ring protons at (6.83-7.506)δ, (2.11-3.29) δ of (CH_3-C=C, CH_3-C=N) protons, (5.78.) δ of thiazine ring protons, (6.37)δ of NH_2 protons, figure (3-6)

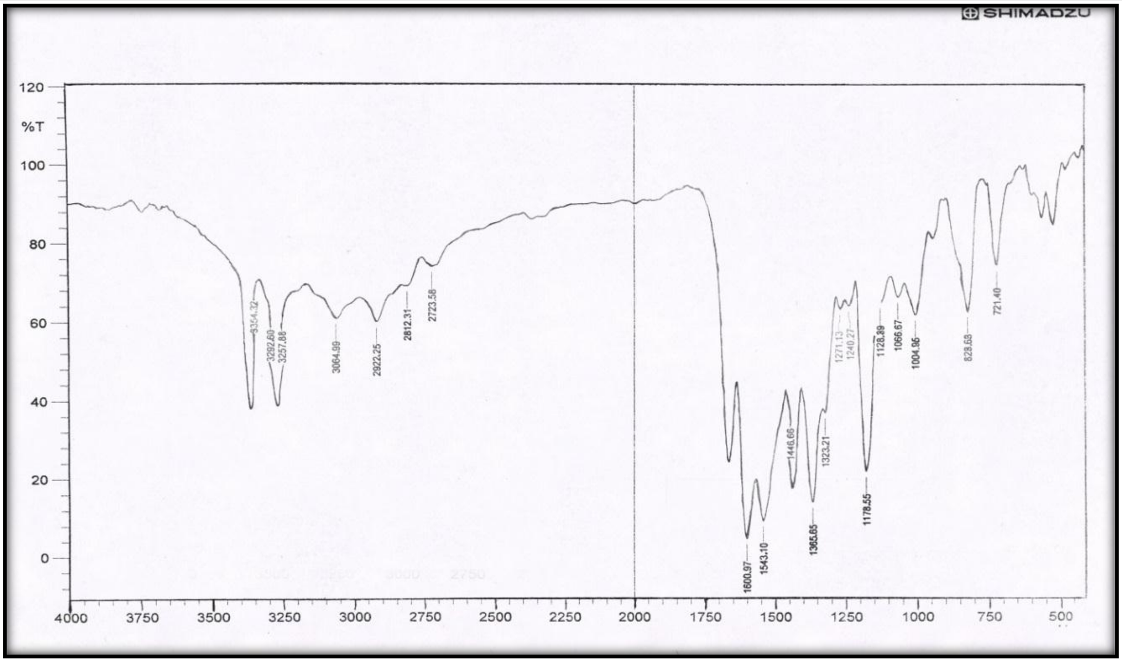


Figure (3-5): FT-IR spectrum in compound A3

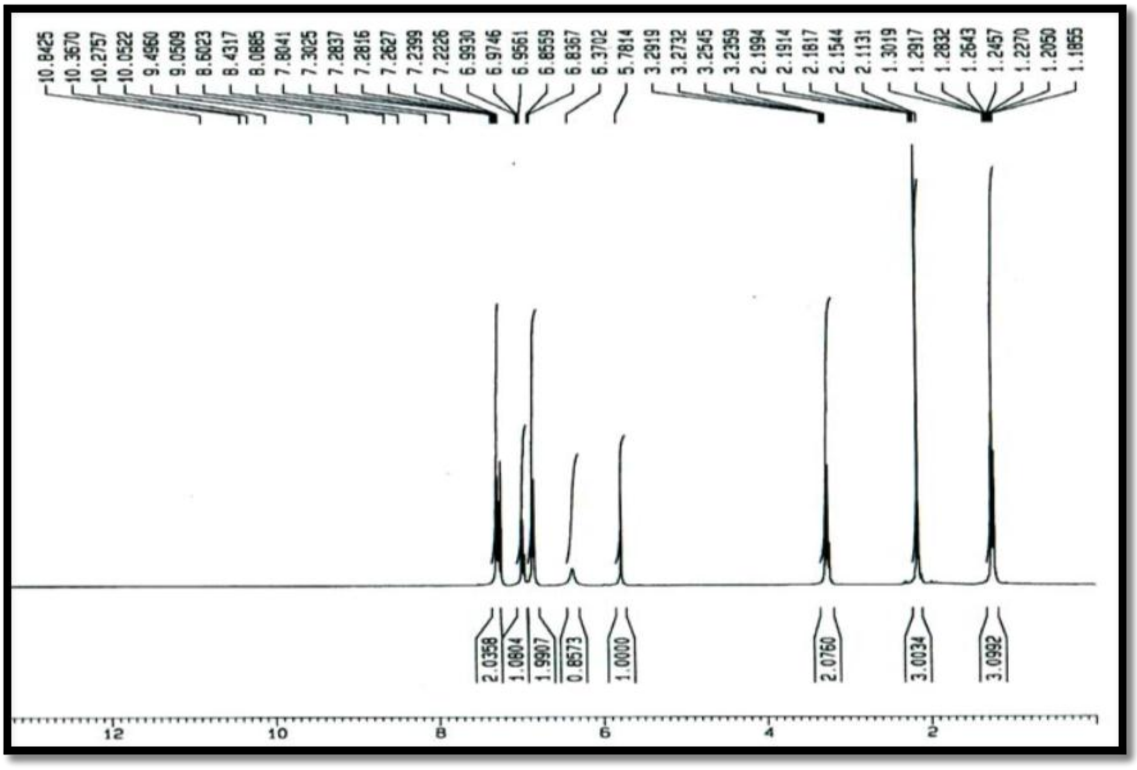


Figure (3-6): ^{1}H-NMR spectrum of compound A3

3.2.4 Synthesis of compound A4

The FT-IR spectrum of compound (A4), The figure (3-7) was showing the disappearance of –N=N- azo group at (1484)cm^{-1} ,shows C=N of inter ring at (1600 – 1647)cm^{-1} , C-H aromatic at (3022 – 3064)cm^{-1}, C-H aliphatic at (2922 – 2989)cm^{-1} , C=C aromatic at 1510cm^{-1}, C-S peaks at 784,824 cm^{-1} , NH_2 of primary amine group at(3281-3354) cm^{-1} .

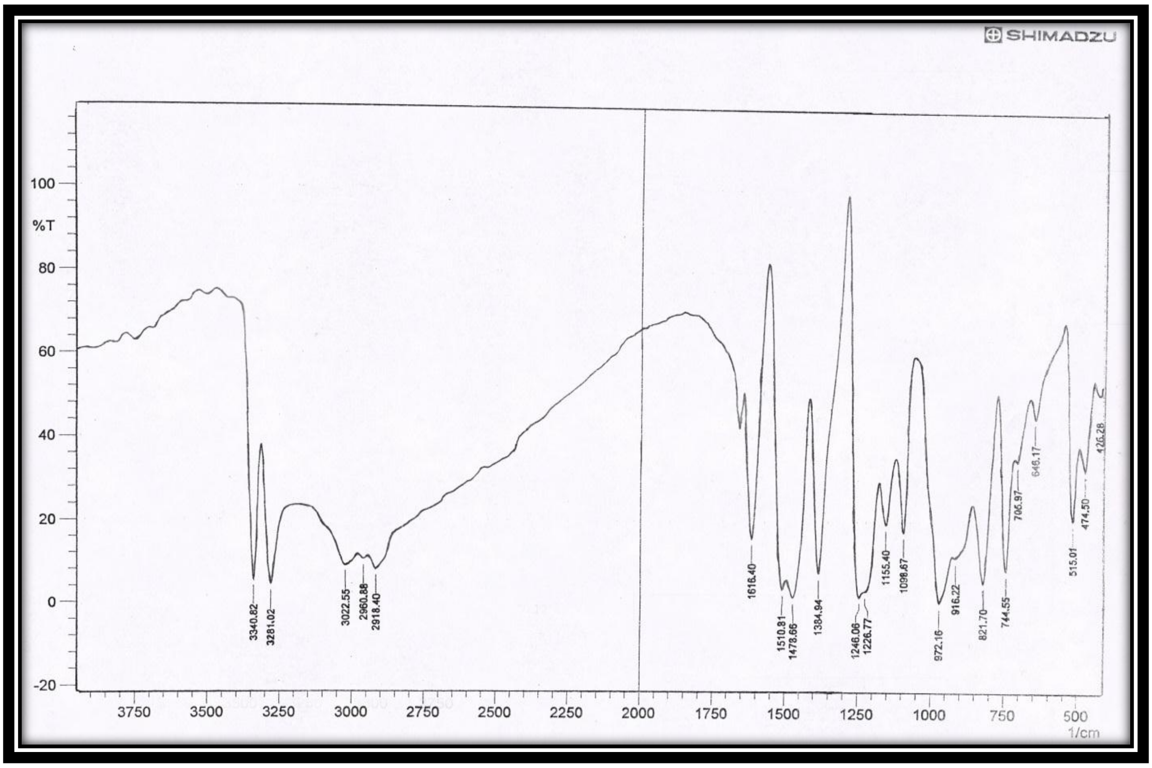


Figure (3-7) FTIR spectrum in compound A4

3-2-5 Synthesis of compound A5

The FT-IR spectrum of compound (A5), figure (3-8) shows disappearance of –N=N- azo group at (1446 – 1494)cm^{-1}, shows C=N of inter ring at (1600 – 1647)cm^{-1} , C-H aromatic at (3022 – 3064)cm^{-1}, C-H aliphatic at (2922 – 2989)cm^{-1} , C-S peaks at (784, 824) cm^{-1}. The ^{13}C-NMR spectrum of compound A5, figure (3-9) was showing disappearance of phenyl ring carbon at (107-137)ppm, appearance thiazine ring carbon atoms at (148-151.6)ppm, CH_3 groups (at 13.47- 36-41) ppm.

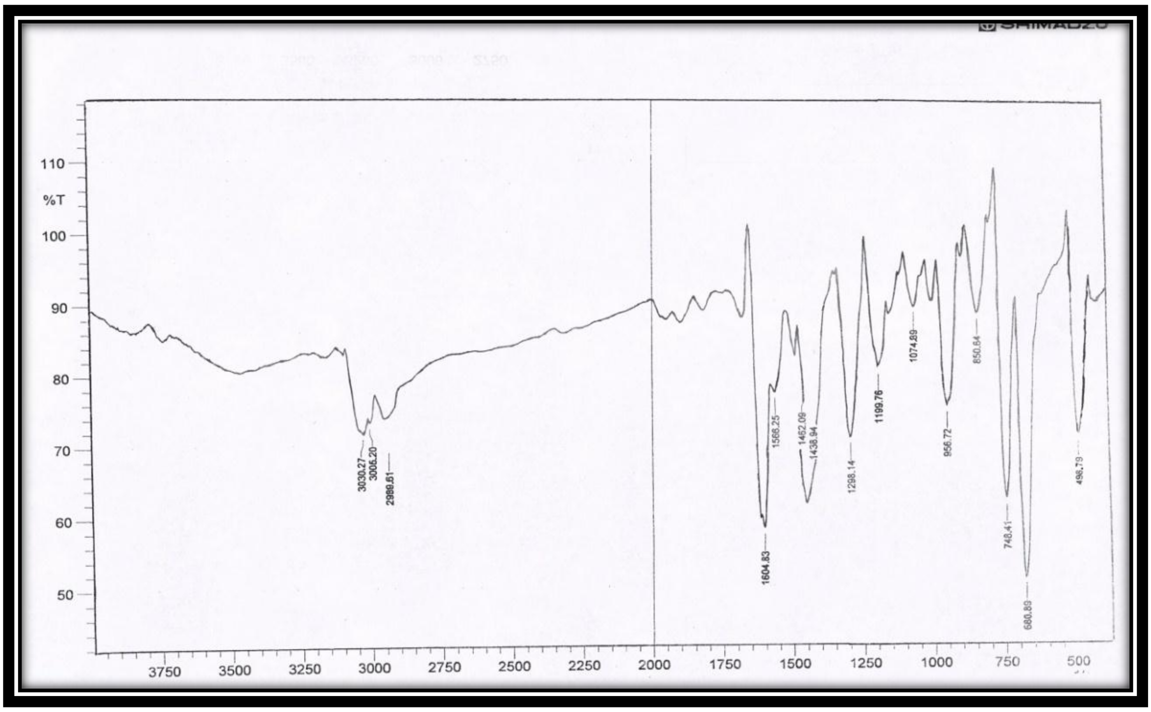


Figure (3-8): FT-IR spectrum in compoundA5

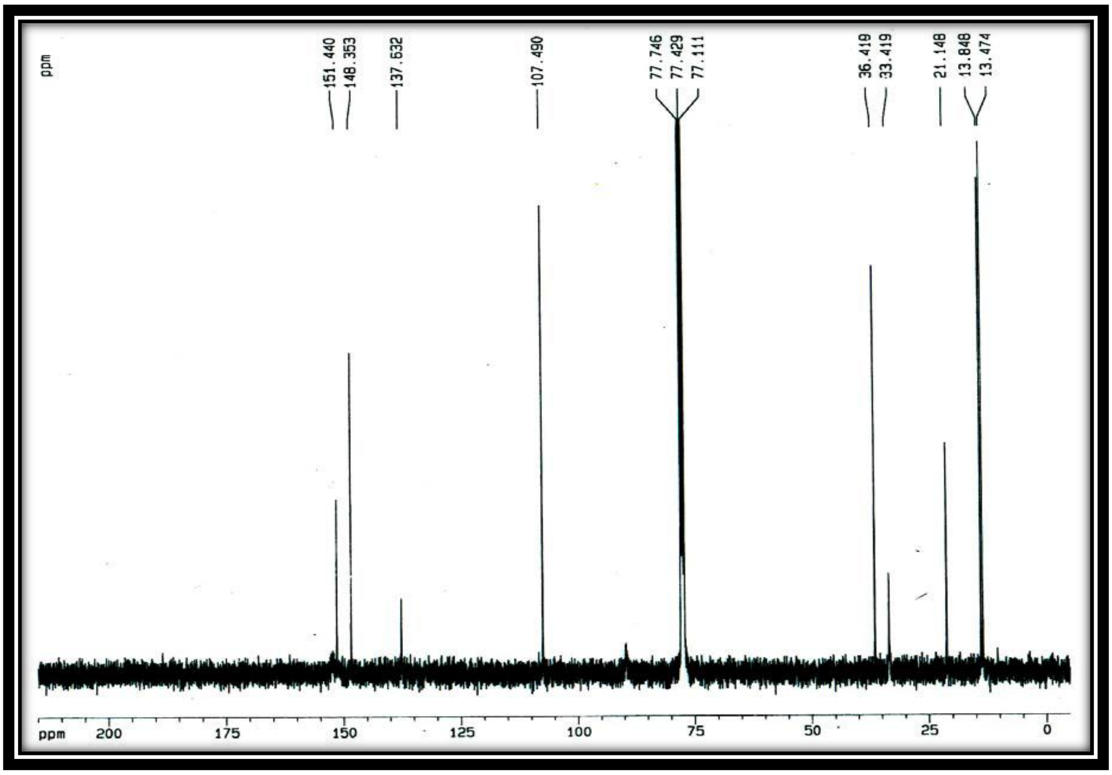


Figure (3-9): ^{13}C-NMR spectrum of compound A5

3-2-6 Synthesis of compound A6

The FT-IR spectrum of compound (A6), The figure (3-10) was showing the appearance S-C at 1188cm^{-1}, C=O of carboxylic acid at (1700-1730)cm^{-1}, OH of carboxylic acid at (2400-3500)cm^{-1} .

The ^{1}H-NMR spectrum of compound (A6), The figure (3-11)was showing the appearance of phenyl ring protons at (7.26-7.816)δ, S-CH_2-CHN protons in the thiazine ring at (2.0-2.50)δ, H-COOH protons at 14.81δ, CH_3-C=N in thiazine ring proton at 3.82δ, CH_3-S of thiazine ring proton at 5.70δ .

The ^{13}C-NMR spectrum of compound A6, The figure (3-12)was showing disappearance of phenyl ring carbon atom at (106-130) ppm, thiazine and thiadiazine ring carbon atoms at (145-163.6) ppm, CH_3 groups at (11.7-22.4) ppm .

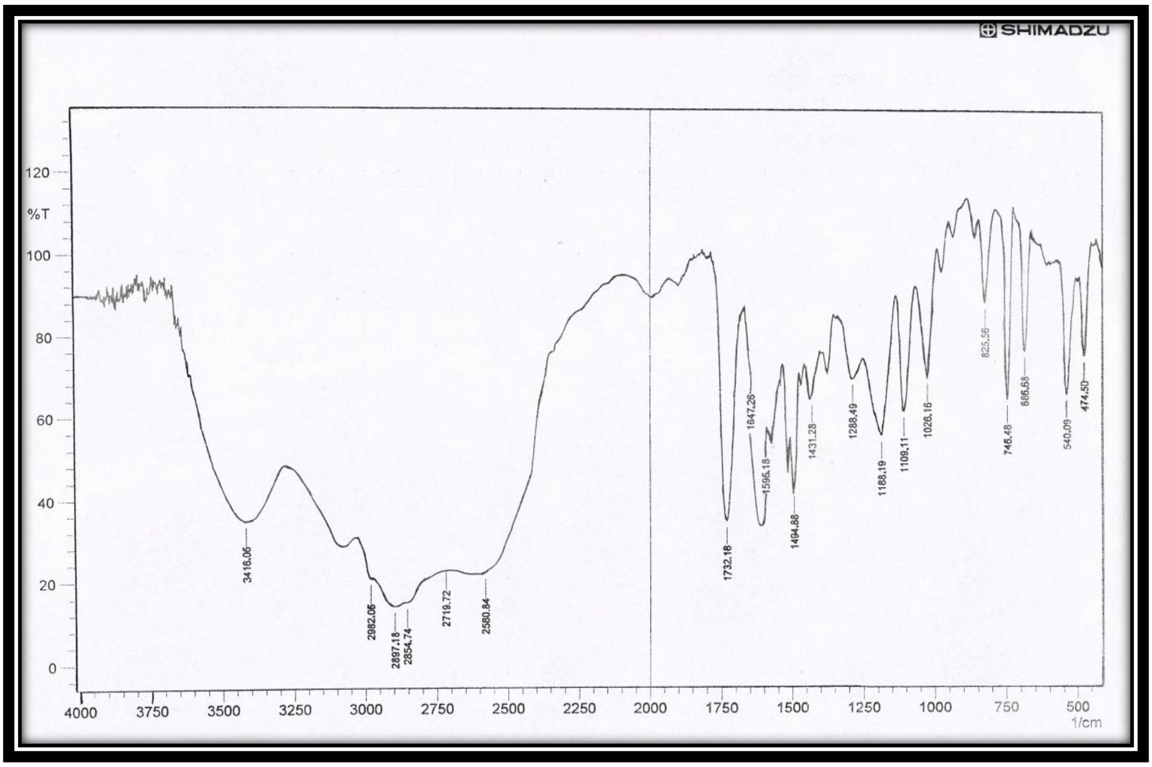


Figure (3-10): FT-IR spectrum of compound A6

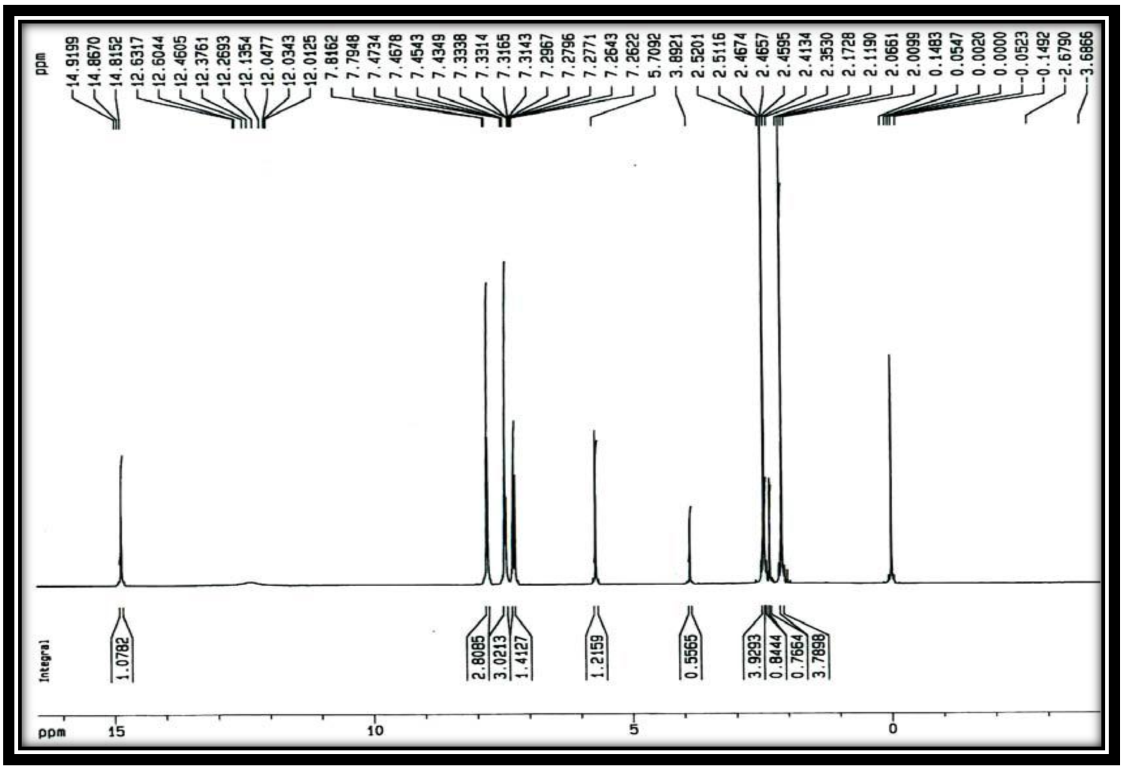


Figure (3-11): ^{1}H-NMR spectrum of compound A6

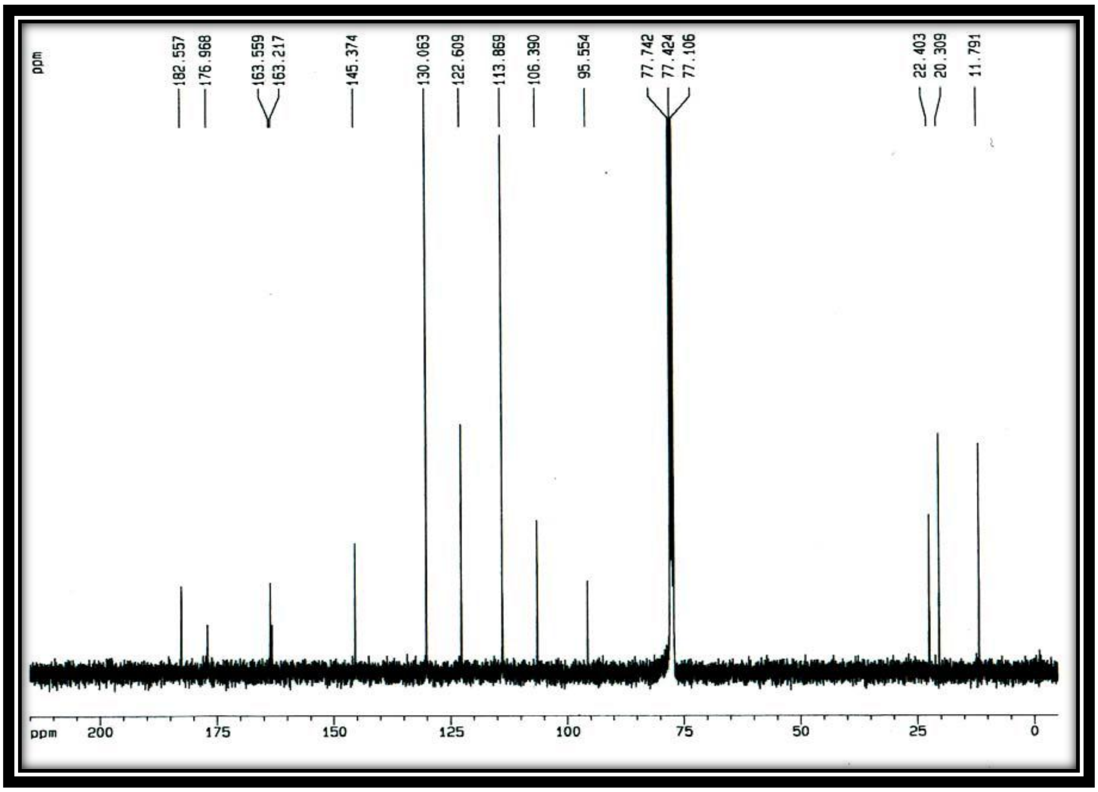


Figure (3-12): ^{13}C-NMR spectrum of compound A6

3-2-7 Synthesis of compound A7

The FT-IR spectrum of compound A7, The figure(3-13) was showing the appearance of inside C=N at (1616-1620) cm^{-1}, C-S at 821 cm^{-1}, C-H aromatic at 3022cm^{-1}, NH_2 of primary amine group at (3178-3281)cm^{-1}.

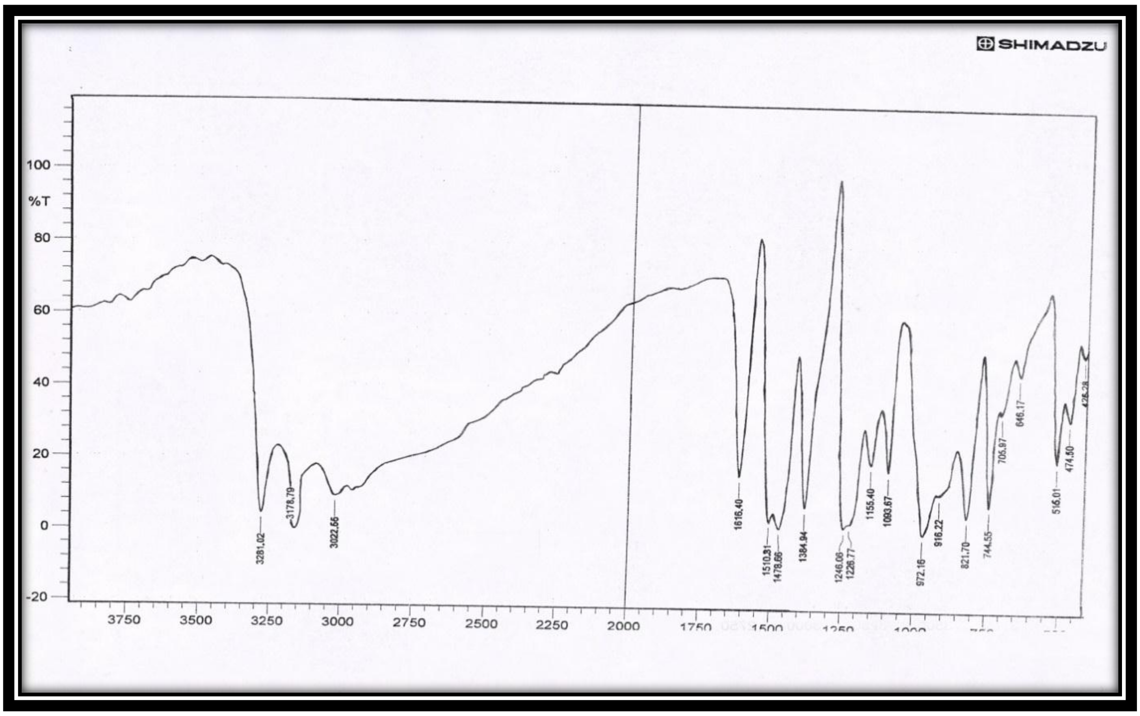


Figure (3-13) : FT-IR spectrum of compound A7

3-2-8 Synthesis of compound A8

The FT-IR spectrum of compound A8, The figure (3-14)was showing appearance of inside C=N at (1640-1690) cm^{-1} , C-S at 831 cm^{-1} , C-H aromatic at 3205 cm^{-1} , SO_2 at 1350 cm^{-1} , (-CO-N) of carbonyl amide groups at 1672 cm^{-1}.

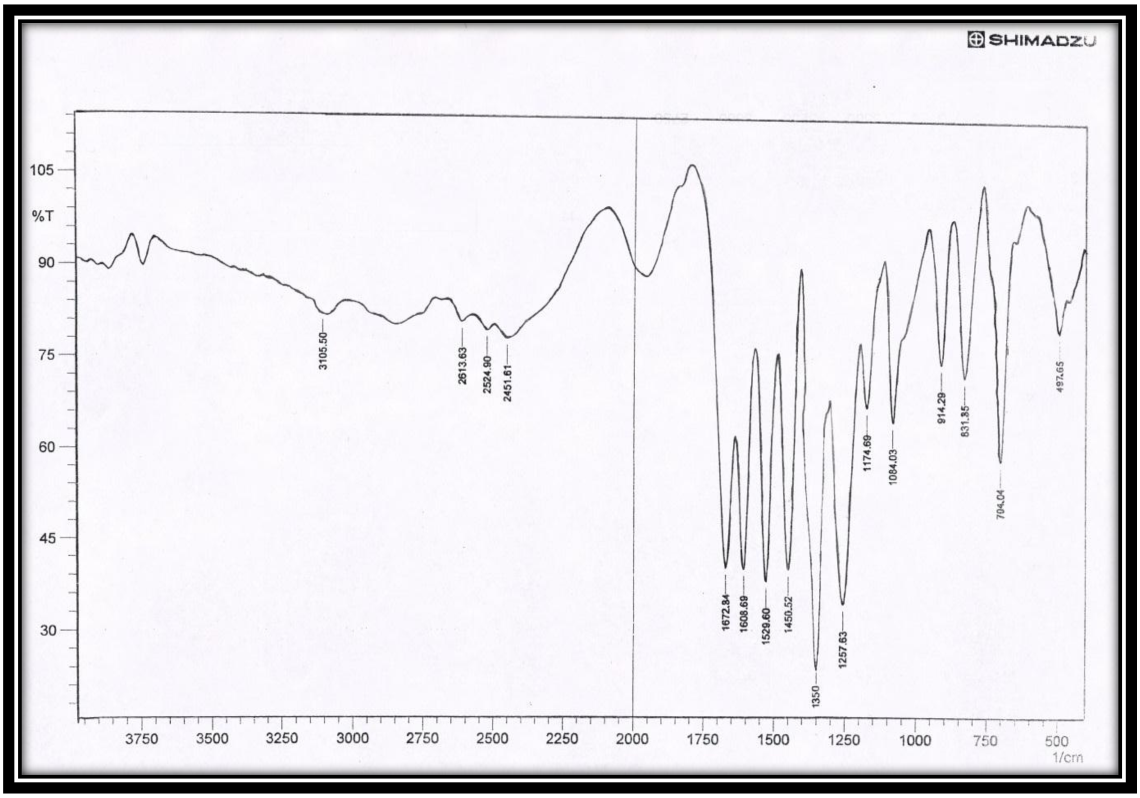


Figure (3-14): FT-IR spectrum of compound A8

3-2-9 Synthesis of compound A9

The FT-IR spectrum of compound A9, The figure(3-15) was showing the appearance of end cyclic C=N at (1616-1620) cm^{-1}, C-H aromatic at 3022cm^{-1}, C-H aliphatic at 2918 cm^{-1}, C-S at 821cm^{-1}, S-C at 1226 cm^{-1}, (CO) carbonyl of carboxylic acid at (1734) cm^{-1}, (O-H) of carboxylic acid at (2590- 3178) cm^{-1} .

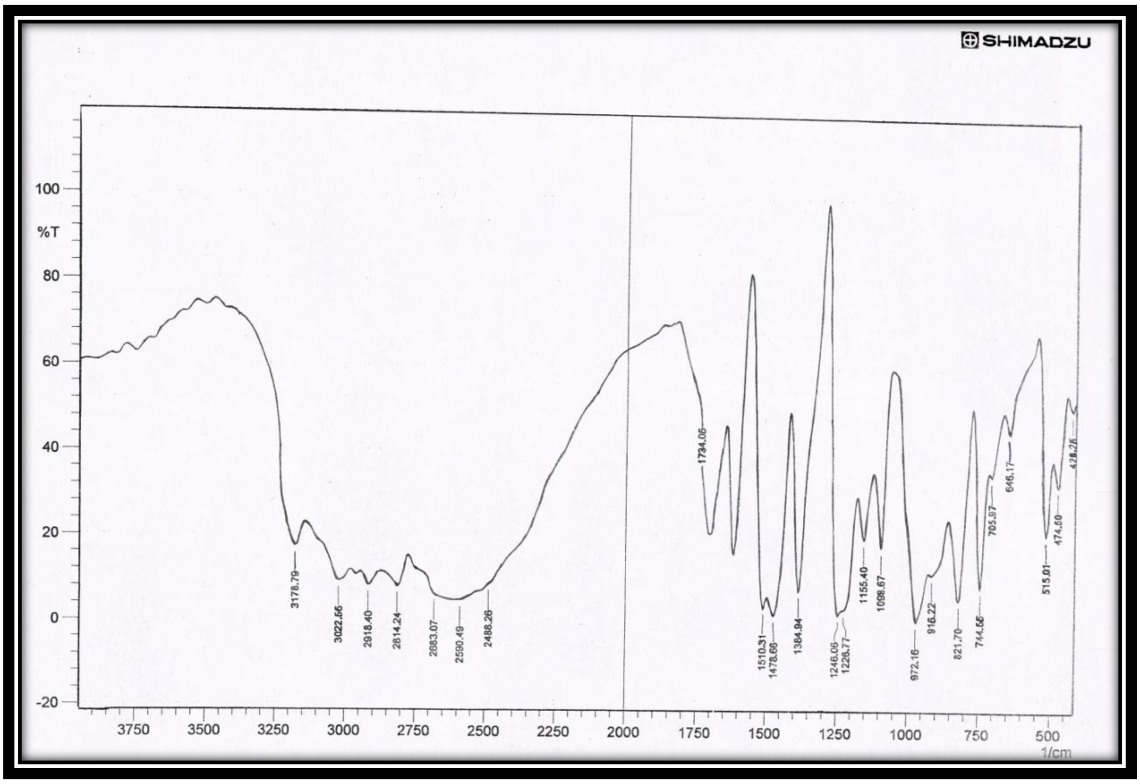


Figure (3-15): FT-IR spectrum of compound A9

3-2-10 Synthesis of compound A10

The FT-IR spectrum of compoundA10, The figure (3-16) was showing the appearance of primary amine group NH_2 at (3338 -3419) $cm^{-1}$and the disappearance of carboxylic acid group, C=N (ring inter) at (1600 -1626) cm^{-1} , C-S at 818cm^{-1} , C-H aliphatic at 2908 cm^{-1} , C-H aromatic at 3000 cm^{-1}.

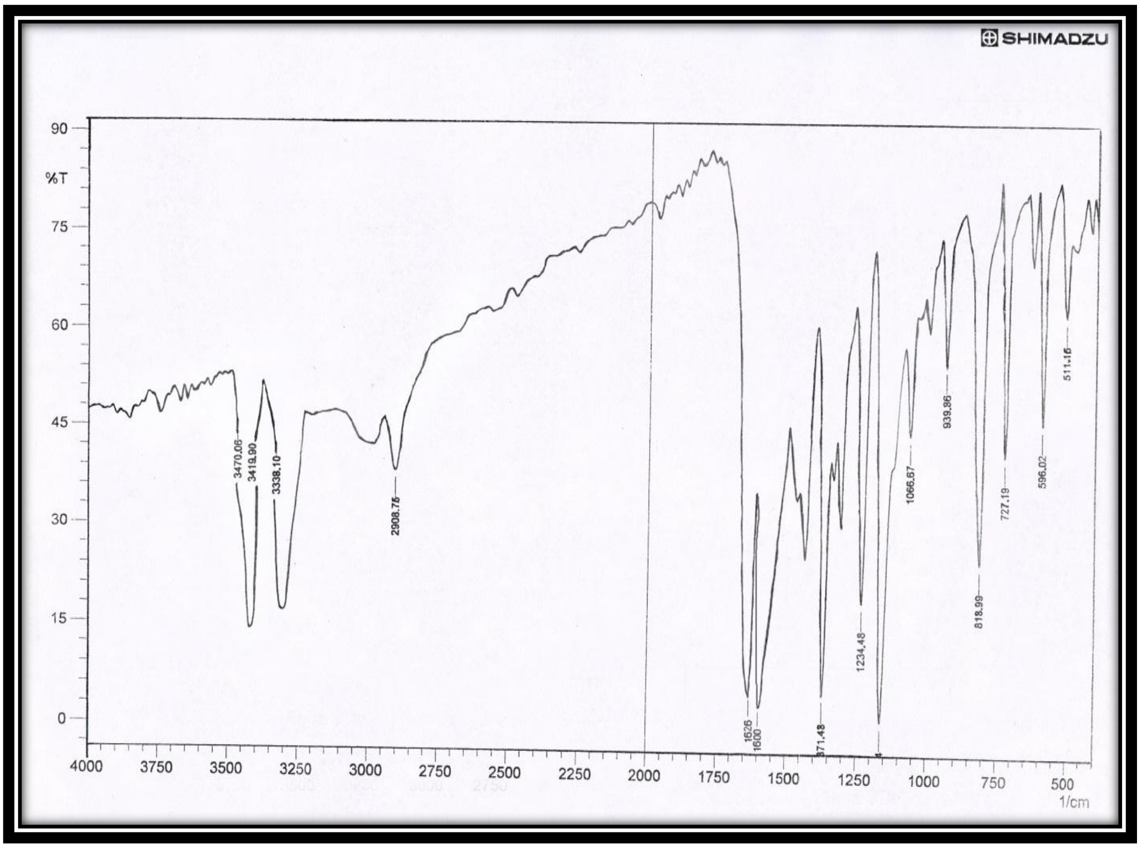


Figure (3-16): FT-IR spectrum in compound A10

In general the FT-IR spectrum, showing the disappearance the peak of C=N at (1600-1626)cm^{-1} in compounds A3, A4, A5, A6, A7, A8, A9 and A10, and the peak of C-H aromatic at (3000- 3064)cm^{-1} in compounds A3, A4, A5, A6, A7, A8, A9 and A10, and the peak of C-H aliphatic at (2922-2908)cm^{-1} in compounds A3, A4, A5, A6, A9 and A10, and the peak of C-S at (748-818)cm^{-1}in compounds A3, A4, A5, A7, A8, A9 and A10, and the peak of NH_2 in compounds A3, A4, A7 and A10, and the peak of (S-CH_2) in compounds A6 and A9, and the peak of (CO) carbonyl of carboxylic acid in compounds A6 and A10, and the peak of O-H of carboxylic acid in compounds A6 and A10, and the peak of N=N azo- group in compounds A3, A4, A5 and A6 .

Table (3-1): Element Analysis heterocyclic sulfur of the prepared compounds

Comp.	M.F	C.H.N.S			
		%S_{calc}	% N_{calc}	%H_{calc}	%C_{calc}
		%S_{found}	%N_{found}	%H_{found}	%C_{found}
A1	$C_{15}H_{13}N_3S$	11.985	15.730	4.869	67.416
		11.612	15.730	4.543	67.013
A2	$C_{20}H_{18}N_4O_2S$	8.466	14.815	4.762	63.492
		8.201	14.394	4.412	63.184
A3	$C_{21}H_{20}N_6S_2$	15.238	20.000	4.762	60.000
		15.081	19.736	4.583	59.650
A4	$C_{21}H_{19}N_7S_2$	14.781	22.633	4.388	58.199
		14.412	22.375	4.116	58.020
A5	$C_{22}H_{21}N_5S_2$	15.274	16.706	5.012	63.007
		15.077	16.367	4.948	62.875
A6	$C_{23}H_{21}N_5O_2S_2$	13.823	15.119	4.536	59.611
		13.601	15.004	4.249	59.324
A7	$C_{10}H_8N_6S_2$	23.188	30.435	2.899	43.478
		23.098	30.301	2.714	43.195
A8	$C_{24}H_{12}N_6O_6S_4$	21.053	13.816	1.974	47.368
		20.928	13.538	1.648	47.174
A9	$C_{14}H_{12}N_2O_4S_2$	19.048	8.333	3.571	50.000
		18.896	8.114	3.284	49.780
A10	$C_{16}H_{14}N_8S_4$	28.700	25.112	3.139	43.049
		28.413	25.032	3.004	42.824

3.3 Flame retardant measurements

3.3.1 Introduction

The unsaturated polyester resins are considered to be moderately flame and inflammable compared to other polymers of the same class, where literature indicate that [121- 125] the LOI for unsaturated polyester resin is 20.6 compared with melamine-formaldehyde resin which is slow flammable and has the limiting oxygen index (LOI) of 42.8 and limiting oxygen index of Phenol- formaldehyde resin is 35.0 . On the other hand, the unsaturated polyester resin has less flammability than some thermoplastic polymers, such as polyethylene (LOI) which is (17.4) and polystyrene (18.1), as well as for some thermally rigid polymers (Thermoplastic polymers), such as epoxy resin which (LOI) are (19.6). Because unsaturated polyester and epoxy resins have been used in various areas of life, many chemical compounds have been used to reduce their ignition, such as halogen compounds as bromine and chlorine compounds. Halogen compounds may be used alone or through synergistic action with oxides Antimony (Sb_2O_3), Phosphorus compounds [126-128].

In this work, the ASTM test results showed that additives which prepared have high efficiency in inhibition of the inflammability of unsaturated polyester ester and epoxy resins. For the purpose of determining the optimal conditions shown by the additives used in the research to the flame inhibition and increase the resistance of combustion of unsaturated polyester and epoxy resin, the results obtained from the standard tests should be reviewed as follows:

3.3.2 Measurements of Limiting oxygen index (LOI)

This method is an important standard test method which is widely using to measure the efficiency of flame retardants. The limiting oxygen index (LOI) represents the ratio of oxygen in the oxygen-nitrogen mixture directed to the burning sample column, which is required for the continuous ignition of the sample for a period of more than three minutes or 100 mm at least [111] .

3.3.2.1 Limiting oxygen index (LOI) of unsaturated polyester resin

The figure (3-17) was showing the increase of the limiting oxygen index (LOI) with increasing of the percentage of the additives in the unsaturated polyester resin. The increasing in the limiting oxygen index (LOI) indicates a decrease in the flammability of the unsaturated polyester resin. The additives act an inert atmosphere in the flame zone due to dissociation of additives with polymer flammability, which can prevent ignition to reduce ignition and provide a inert layer or act a barrier to oxygen, reducing and preventing the arrival of oxygen necessary to continue the flame .

Table (3-2) showing the results of the measurement of the limiting oxygen index (LOI) of the unsaturated polyester resin, by the use of different additives and at the percentage of weight ranging from (0.2– 0.8 %), through which it can be concluded that the efficiency of the compounds added to the increase in the limiting oxygen index (LOI), shall be in the following order:

A10 > A4 > A8 > A3 > A7 > A6 > A5 > A2 > A1 > A9

Table (3-2): (LOI) for unsaturated polyester resin with additives

LOI Additives	LOI %				
	Non	0.2	0.4	0.6	0.8
A1	20.6	21.46	21.92	22.61	23.21
A2	20.6	21.72	22.45	22.97	23.62
A3	20.6	22.84	23.53	24.38	25.14
A4	20.6	23.71	24.56	25.46	26.31
A5	20.6	21.97	22.69	23.24	23.95
A6	20.6	21.98	22.70	23.25	23.96
A7	20.6	22.41	23.12	23.91	24.62
A8	20.6	23.40	24.18	24.96	25.74
A9	20.6	21.14	21.70	22.30	22.86
A10	20.6	23.96	24.81	25.79	26.89

It is clear from the results of the tests of the limiting oxygen index of the unsaturated polyester resin and using the additives which prepared in this work. It is the effective in inhibition of flammability and increasing the resistance of flame of unsaturated polyester resin, through the amount of oxygen required to continue the resin formation for three minutes or the continuation of the 50 mm at least, which leads to increase in inhibition by increasing the percentage of weight of the additives, which indicates the effectiveness of these compounds in inhibition compared with what is written in the literature. The oxygen concentration of the unsaturated polyester resin alone is (20.6), but the LOI is equal to (26.89) when a 0.8% percentage of compound (A 10) is used as an addition to flame retardant because it contains an increase of free radicals ($N^{\bullet}$ and $S^{\bullet}$), which is effective in flame retardant.

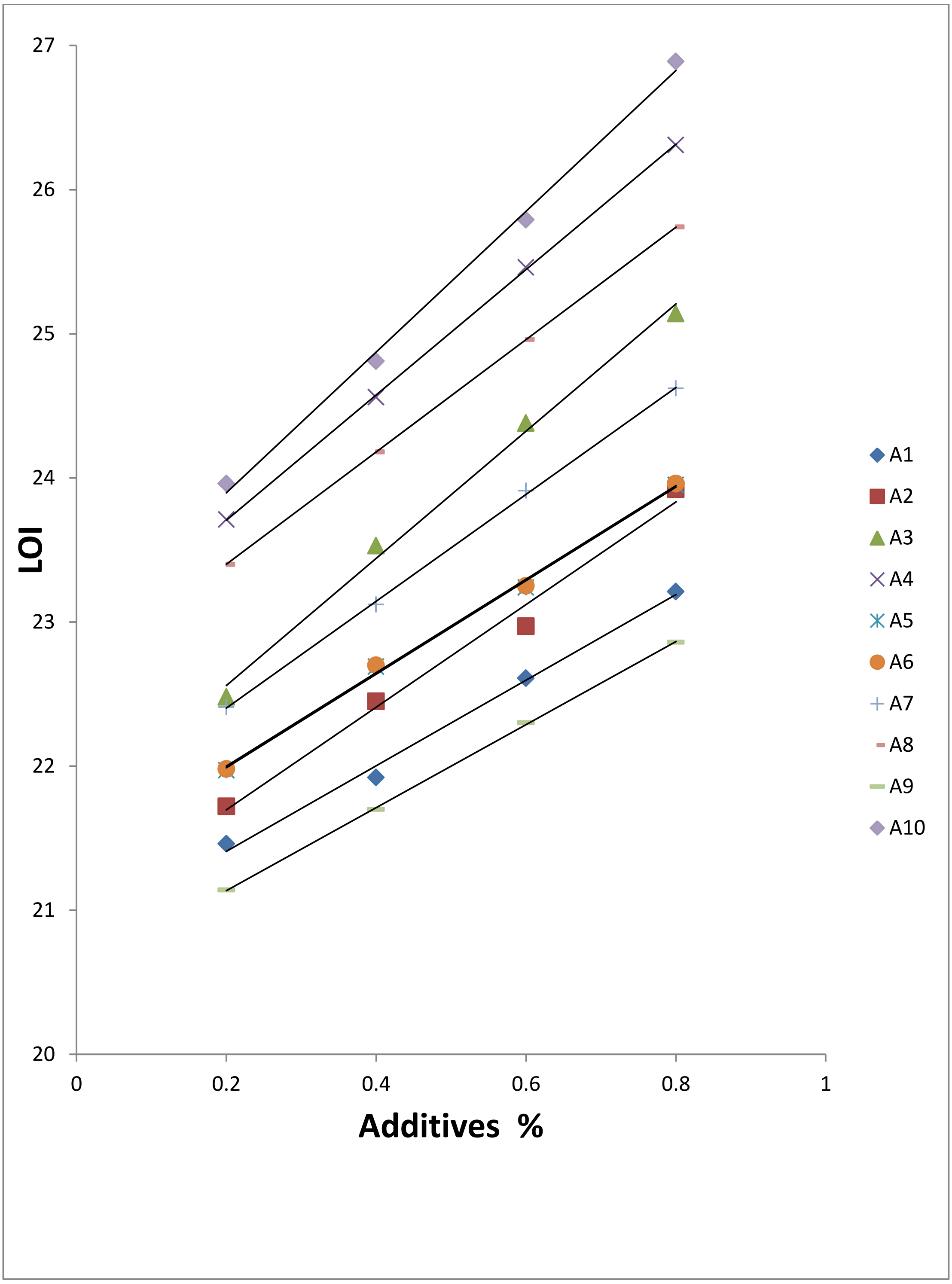


Figure (3-17): Limiting Oxygen Index (LOI) for unsaturated polyester resin with different percentage of additives

3.3.2.2 Measurement of the limiting oxygen index of epoxy resin

The figure (3-18) is showing the increasing of the limiting oxygen index (LOI) with the increasing in the percentage of the weight of the additives in the epoxy resin. The increasing in the limiting oxygen index (LOI) indicates a reduction of the flammability in the epoxy resin, where the additives create an inert atmosphere in the flame zone due to dissociation of additives with polymer flammability, which can prevent ignition to reduce ignition and provide a inert layer or act as a barrier to oxygen, reducing and preventing the arrival of oxygen necessary to continue the flame.

Table (3-3): Limiting oxygen index (LOI) for epoxy resin with additives

LOI Additives	LOI %				
	Non	0.2	0.4	0.6	0.8
A1	19.6	20.51	21.16	21.73	22.35
A2	19.6	20.84	21.43	22.08	22.61
A3	19.6	21.73	22.62	23.71	24.46
A4	19.6	22.17	23.41	24.63	25.28
A5	19.6	21.01	21.82	22.47	23.15
A6	19.6	21.03	21.84	22.48	23.16
A7	19.6	21.42	22.31	23.26	24.05
A8	19.6	21.90	23.00	23.98	24.72
A9	19.6	20.32	20.91	21.48	22.03
A10	19.6	22.41	23.83	24.91	25.64

The table (3-3) is showing the results of the measurements of the limiting oxygen index (LOI) of epoxy resin using different additives and at the weight percentage of ranging from (0.2 - 0.8 %). It can be concluded that the efficiency of the compounds added to the increase in limiting oxygen index (LOI) and reducing the flammability and increasing the resistance of ignition and be in the following order:

A10 > A4 > A8 > A3 > A7 > A6 > A5 > A2 > A1 > A9

It is clear from the results of the tests of the limiting oxygen index of epoxy resins which used in this work that its effectiveness in inhibiting the flame and increasing of the resistance of epoxy resin, through the amount of oxygen required for the continuation of ignition the resin. The limiting oxygen index (LOI) of the epoxy resin alone is equal to 19.7, while the limiting oxygen index (LOI) is equal to 20.32 when used of 0.2% of the additive A9. The limiting oxygen index (LOI) is equal to 25.64 when using the concentration of 0.8% of compound A10. The results in the two tables correspond with the conclusions of Fretz and Green , where the limiting oxygen index (LOI) for unsaturated polyester and epoxy resins without additives is equal to (20.6) and (17.9) respectively.

The increasing of the limiting oxygen index (LOI) of resin containing of different weight percentages of additives can be attributed to the release of hydrogen free radicals which removes the active free radicals in the flame chain and also inhibits the process of thermal fragmentation that occurs in the front of the flame due to its effect Reduce the amount of heat generated by the flame, in addition to forming a group of non-flammable gases such as H_2O, CO_2 and CO, that reduce volatile flammable substances and provide an oxygen-free atmosphere and burnt zone, and the char which formed of thermal analysis is a barrier that protects the polymer from heat.

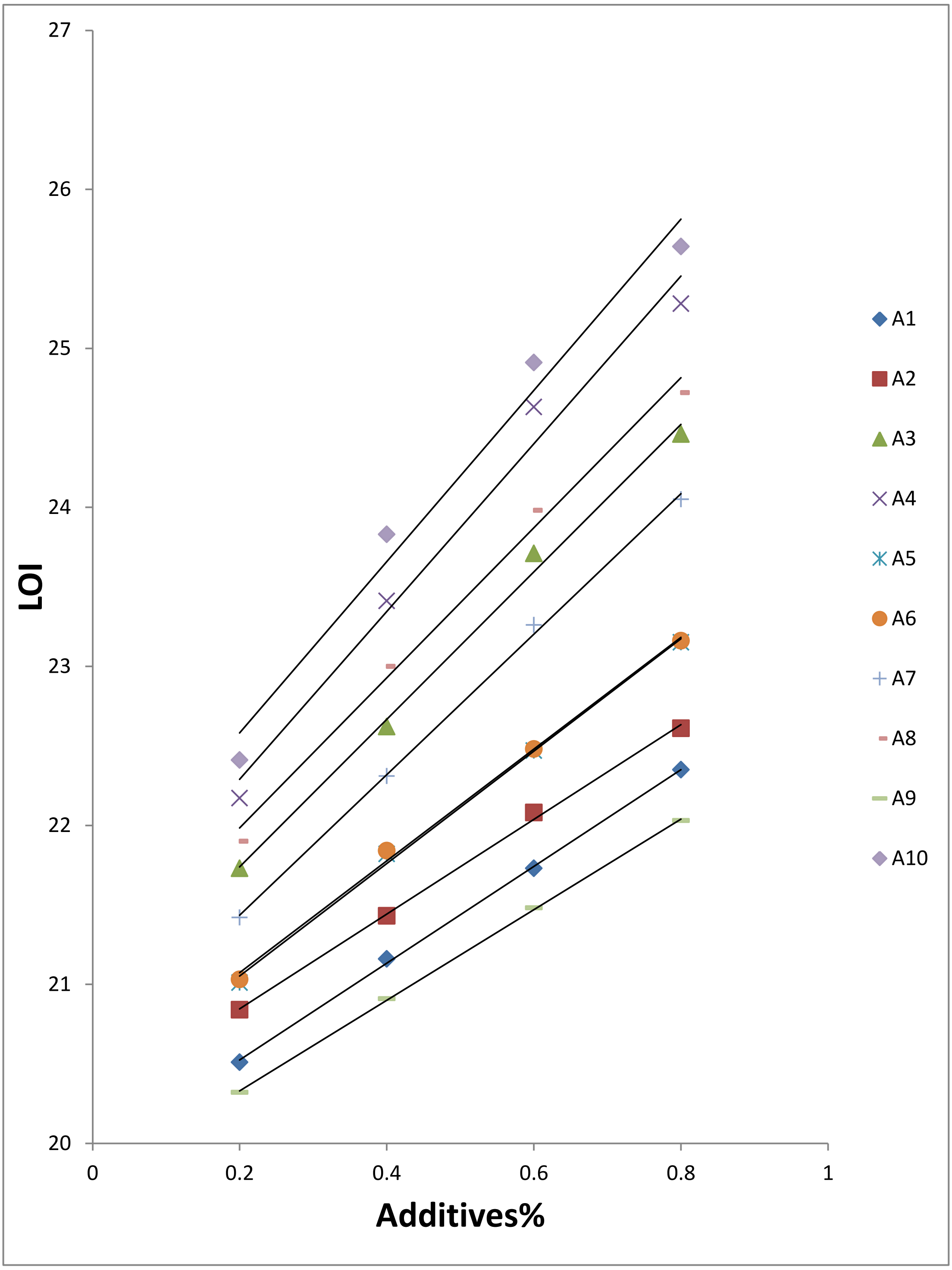


Figure (3-18): Limiting Oxygen Index (LOI) for epoxy resin with different percentage of additives

3.3.3 Measurements of flame propagation speed

3.3.3.1 Flame propagation speed of unsaturated polyester resin

The results of flame propagation are speed showing a high decreasing in the rate of burning (RB) for unsaturated polyester resin, as shown in tables (3-4) to (3-13), where the rate of burning for the unsaturated polyester resin samples were measured without additive and then using additives according to the standard method test ASTM: D-635. Rate of burning showed decreases with increasing of weight percentage of additives (inversely proportional), as indicated in figure (3-19).

The measurements showed that the best effective ratio of additives for inhibition of unsaturated polyester resin was (0.2%) for additive (A10). This ratio led to self-extinguishing of unsaturated polyester resin after (8.262) minutes of source thermal dimensions and the rate of burning (RB) was equal to (0.65) cm / min as shown in the table (3-13).

From the above, it can be said that the efficiency of additives used to inhibit the flame propagation speed of unsaturated polyester resin takes the following sequence:

A10 > A4 > A8 > A3 > A7 > A6 > A5 > A2 > A1 > A9

These results are consistent with the results obtained from the measurement of the limiting oxygen index (LOI).

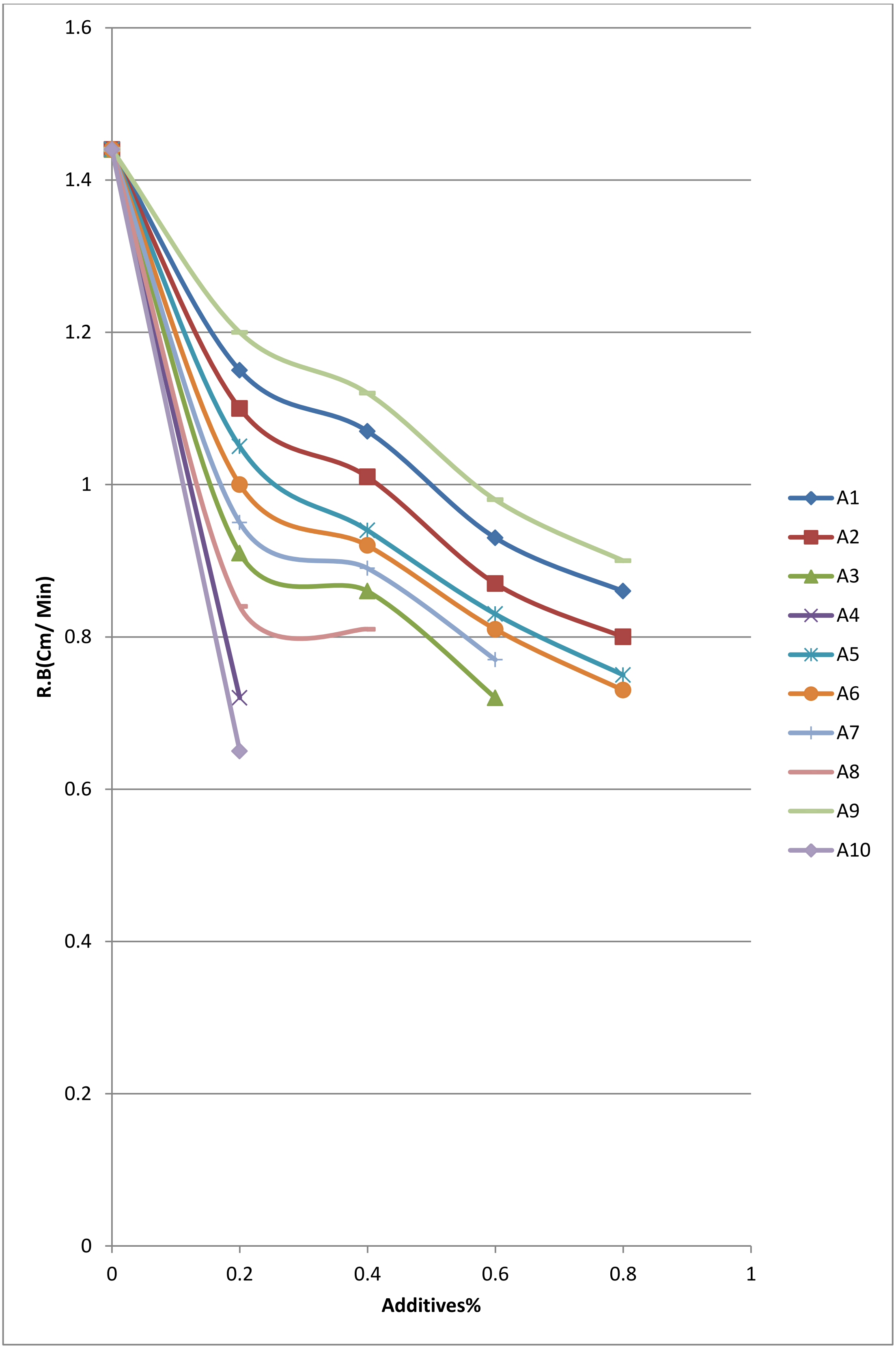


Figure (3-19): The rate of burning (R.B) for unsaturated polyester with different weight percentage of additives

Table (3-4): (R.B.) for unsaturated polyester resin with additive A1

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	10	9.46	9.18
ATB (Min.)	6.92	8.645	9.345	10.172	10.674
R.B. (cm./ Min.)	1.44	1.15	1.07	0.93	0.86
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-5): (R.B.) for unsaturated polyester resin with additive A2

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	10	8.52	8.00
ATB (Min.)	6.92	9.091	9.901	9.793	10.000
R.B. (cm./ Min.)	1.44	1.10	1.01	0.87	0.80
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-6): (R.B.) for unsaturated polyester resin with additive A3

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	8.12	7.52	-
ATB (Min.)	6.92	10.990	9.442	10.444	-
R.B. (cm./ Min.)	1.44	0.91	0.86	0.72	-
S.E	-	-	yes	yes	yes
N.B.	-	-	-	-	yes

Table(3-7): (R.B.) for unsaturated polyester resin with additive A4

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	5.79	-	-	-
ATB (Min.)	6.92	8.042	-	-	-
R.B. (cm./ Min.)	1.44	0.72	-	-	-
S.E	-	yes	yes	yes	yes
N.B.	-	-	yes	yes	yes

Table (3-8): (R.B.) for unsaturated polyester resin with additive A5

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	10	9.64	8.28
ATB (Min.)	6.92	9.524	10.628	11.614	11.040
R.B. (cm./ Min.)	1.44	1.05	0.94	0.83	0.75
S.E	-	-	-	-	yes
N.B.	-	-	-	-	-

Table(3-9): (R.B.) for unsaturated polyester resin with additive A6

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	10	9.27	8.42
ATB (Min.)	6.92	10.000	10.869	11.444	11.534
R.B. (cm./ Min.)	1.44	1.00	0.92	0.81	0.73
S.E	-	-	-	-	yes
N.B.	-	-	-	-	-

Table(3-10): (R.B.) for unsaturated polyester resin with additive A7

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	9.25	8.13	-
ATB (Min.)	6.92	10.526	10.393	10.558	-
R.B. (cm./ Min.)	1.44	0.95	0.89	0.77	-
S.E	-	-	-	yes	yes
N.B.	-	-	-	-	yes

Table(3-11) : (R.B.) for unsaturated polyester resin with additive A8

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	8.68	6.72	-	-
ATB (Min.)	6.92	10.334	8.296	-	-
R.B. (cm./ Min.)	1.44	0.84	0.81	-	-
S.E	-	-	yes	yes	yes
N.B.	-	-	-	yes	yes

Table(3-12): (R.B.) for unsaturated polyester resin with additive A9

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	9.16	7.93	7.37
ATB (Min.)	6.92	8.333	8.178	8.092	8.189
R.B. (cm./ Min.)	1.44	1.20	1.12	0.98	0.90
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table (3-13): (R.B.) for unsaturated polyester resin with additive A10

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	5.37	-	-	-
ATB (Min.)	6.92	8.262	-	-	-
R.B. (cm./ Min.)	1.44	0.65	-	-	-
S.E	-	yes	yes	yes	yes
N.B.	-	-	yes	yes	yes

3.3.3.2 Flame propagation speed of epoxy resin

The results of flame propagation speed showed a high decrease in rate of burning (RB) for epoxy resin, as shown in tables (3-14) to (3-23), where the rate of burning for the epoxy resin samples was measured without additive and then using additives according to the standard method test ASTM: D-635. Rate of burning showed decreases with increasing of weight percentage of additives (inversely proportional), as indicated in figure (3-20).

The measurements showed that the best effective ratio of additives for inhibition of epoxy resin was (0.2%) for additive (A10). This ratio led to self-extinguishing of epoxy resin after (14.545) minutes of source thermal dimensions and the rate of burning (RB) was equal to (0.55) cm / min as shown in the table (3-23).

From the above, it can be said that the efficiency of additives used to inhibit the flame propagation speed of epoxy resin takes the following sequence:

A10 > A4 > A8 > A3 > A7 > A6 > A5 > A2 > A1 > A9

These results are consistent with the results obtained from the measurement of the limiting oxygen index (LOI).

Table(3-14): (R.B.) for epoxy resin with additive A1

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	10	9.4	8.8
ATB (Min.)	5.12	6.211	6.535	6.812	7.096
R.B. (cm./ Min.)	1.95	1.61	1.53	1.38	1.24
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-15): (R.B.) for epoxy resin with additive A2

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	10	8.7	8.1
ATB (Min.)	5.12	6.810	7.194	6.960	7.297
R.B. (cm./ Min.)	1.95	1.47	1.39	1.25	1.11
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-16): (R.B.) for epoxy resin with additive A3

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	9.0	7.6	6.8	-
ATB (Min.)	5.12	8.653	7.920	8,293	-
R.B. (cm./ Min.)	1.95	1.04	0.96	0.82	-
S.E	-	-	-	yes	yes
N.B.	-	-	-	-	yes

Table(3-17): (R.B.) for epoxy resin with additive A4

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	8.6	5.9	-	-
ATB (Min.)	5.12	10.886	9.672	-	-
R.B. (cm./ Min.)	1.95	0.79	0.61	-	-
S.E	-	yes	yes	yes	yes
N.B.	-	-	-	yes	yes

Table(3-18): (R.B.) for epoxy resin with additive A5

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	9.3	8.5	8.0
ATB (Min.)	5.12	7.520	7.501	7.589	8.247
R.B. (cm./ Min.)	1.95	1.33	1.24	1.12	0.97
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-19): (R.B.) for epoxy resin with additive A6

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	9.0	8.3	7.6
ATB (Min.)	5.12	7.576	7.317	7.477	7.917
R.B. (cm./ Min.)	1.95	1.32	1.23	1.11	0.96
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-20): (R.B.) for epoxy resin with additive A7

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	9.5	8.2	7.5	5.7
ATB (Min.)	5.12	8.051	10.789	7.576	6.760
R.B. (cm./ Min.)	1.95	1.18	1.13	0.99	0.85
S.E	-	-	-	-	yes
N.B.	-	-	-	-	-

Table(3-21): (R.B.) for epoxy resin with additive A8

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	8.8	6.1	4.9	-
ATB (Min.)	5.12	9.462	8.026	7.903	-
R.B. (cm./ Min.)	1.95	0.93	0.76	0.62	-
S.E	-	-	yes	yes	yes
N.B.	-	-	-	yes	yes

Table(3-22) : (R.B.) for epoxy resin with additive A9

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	10	9.3	8.1	7.5
ATB (Min.)	5.12	5.882	5.706	5.510	5.556
R.B. (cm./ Min.)	1.95	1.70	1.63	1.47	1.35
S.E	-	-	-	-	-
N.B.	-	-	-	-	-

Table(3-23): (R.B.) for epoxy resin with additive A10

Tests	Additives %				
	Non	0.2	0.4	0.6	0.8
AEB (cm.)	10	8.0	5.7	-	-
ATB (Min.)	5.12	14.545	11.633	-	-
R.B. (cm./ Min.)	1.95	0.55	0.49	-	-
S.E	-	yes	yes	yes	yes
N.B.	-	-	-	yes	yes

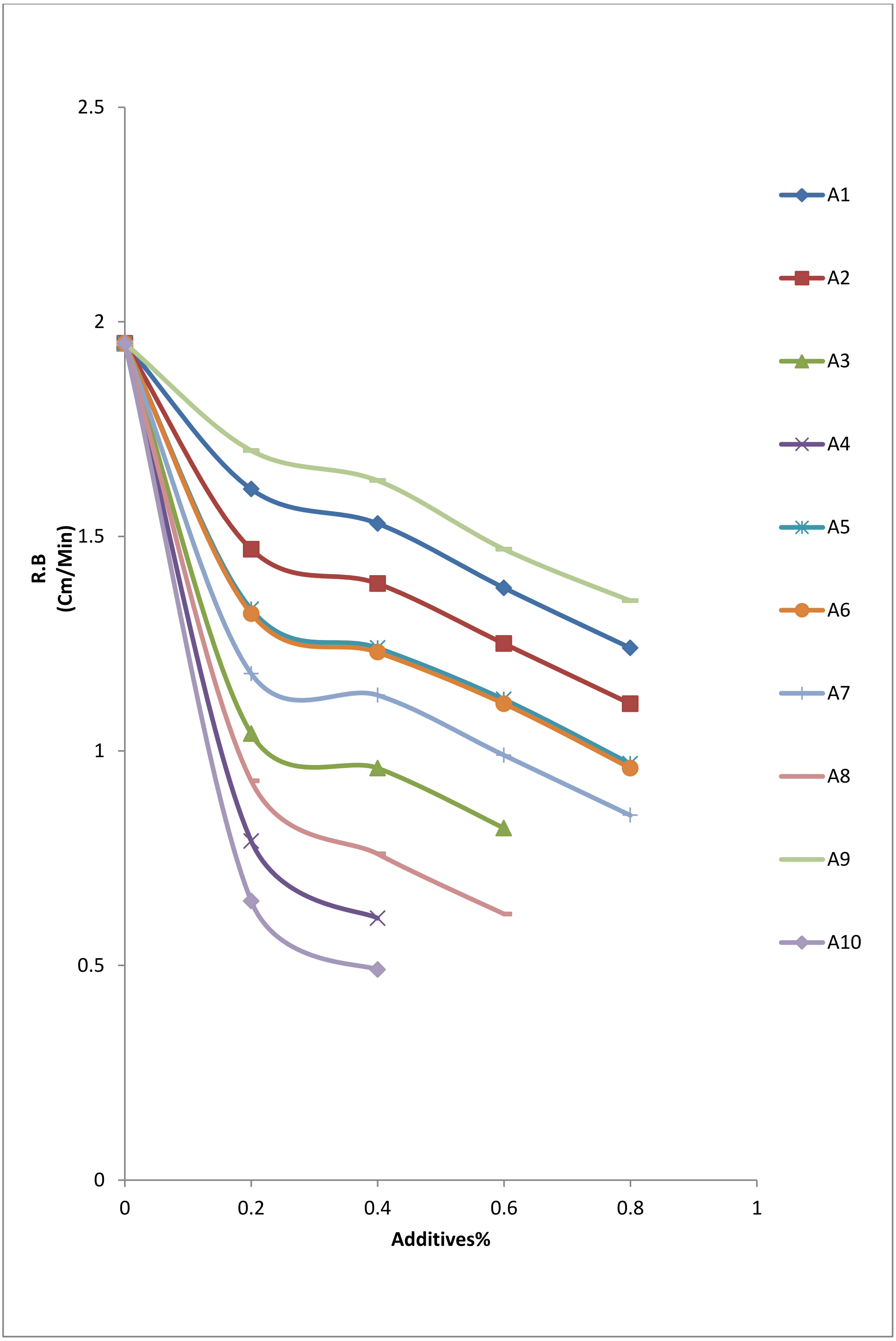


Figure (3-20): The rate of burning (R.B) for epoxy resin with different weight percentage of additives

CHAPTER FOUR

Conclusion
&
Future Works

Conclusion

In view of the fact that the unsaturated polyester and epoxy resins are widely used in many commercial fields, scientific research have tended to find ways to prevent the burning or reduction of ignition of these two resin. Many materials have been used to flammability. The substances used are inorganic compounds such as antimony oxide, borax, phosphorus compounds and many others. Organic compounds have never been overlooked due to their special preparation methods.

In this work, ten of heterocyclic compounds were prepared. These compounds were selected based on the number of nitrogen and sulfur atoms in each of them. Nitrogen and sulfur were chosen as a triangular equivalent, i.e., they can be associated with the three atoms to form a stable compound.

Those compounds have been shown very high effectiveness in inhibition of flame of unsaturated polyester and epoxy resins, much better than the previously inorganic materials.

The Future Work

The following points can be suggested as a plan:

1. The Preparation of heterocyclic compounds containing quadrilateral atoms and their experience in flammability of unsaturated polyester and epoxy resins.

2 - The prepared compounds are used in our research as flame retardants of other resins such as melamine and alkyd resins.

3 – Used other measurements such as the flame high and the density of smoke.

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الخلاصة

في هذا البحث ، حضرت عشرة مركبات عضوية حلقية غير متجانسة ، و درست فعاليتها في تثبيط لهوبية وزيادة مقاومة اشتعال راتنج البولي استر غير المشبع وراتنج الايبوكسي، وهذه المضافات هي:

1. **Additive A1:** (5,6-diphenyl-6H-1,3,4-thiadiazin-2-amine)
2. **Additive A2:** (Pentane -2,3,4-trione3-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)hydrazine])
3. **Additive A3:** (5-[(z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-4,6 dimethyl-2H-1,3-thiazin-2-amine)
4. **Additive A4:** (6-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-5,7 dimethyl -1,3,4-thiadiazepin-2-amine)
5. **Additive A5:** (5,6-diphenyl-2-[(Z)-(2,4,6-trimethyl-2H-1,3-thiazin-5-yl) diazenyl]-6H-1,3,4-thiadiazine)
6. **Additive A6:** ((4Z,6E)-6-((Z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl) diazenyl)-5,7-dimethyl-2,3-dihydro-1,4-thiazepine -3-carboxylic acid)
7. **Additive A7:** (5-(1,4-phenylene)bis (1,3,4-thiadiazinol-2-amine)
8. **Additive A8:** (2,2-(1,4-phenylene-bis-(1,3,4-thiadiazole)-5yl)bis(1,2-benzisothiazol-3(2H)-one) 1,1,1,1,-tetraoxide)
9. **Additive A9:** (2,2-(1,4-phenylene)bis(4,5-dihydro-1,thiazole-4-carboxylic acid)
10. **Additive A10:** (5,5-[1,4-phenylene bis(4,5-dihydro-1.3-thiazole-2,4-diyl) bis (1,3,4-thiadiazol-2-amine))

تم تحضير ثلاثة ألواح بأبعاد (13×13×0.3) سم لكل من راتنج البولي استر غير المشبع مع المضافات أعلاه وكذلك لراتنج الايبوكسي مع الألواح أعلاه ، وبنسب وزنية مئوية (0.2 ، 0.4 ، 0.6 و 0.8 %) ، تم تقطيع هذه الألواح أو الرقائق إلى عينات وبأبعاد مناسبة وحسب طرق القياس المعتمدة (American Society of Testing and Materials) (ASTM).

تضمنت الدراسةً إجراء مجموعة من الفحوصات القياسية المستخدمة لقياس إعاقة اللهوبية وزيادة مقاومة الأشتعال ، تم اختيار طريقتين قياسيتين لبيان مدى كفاءة المضافات في إعاقة لهوبية راتنج البولي استر غير المشبع وراتنج الايبوكسي، وهذه الطرق هي :

١- طريقة قياس معامل الأوكسجين المحدد (LOI) باستخدام طريقة الفحص المعتمدة (ASTM: D-2863).

٢- طريقة قياس سرعة الاحتراق (R.B) ومدى الاحتراق (E.B) والزمن اللازم للاحتراق (TB) من خلال طريقة الفحص المعتمدة (ASTM: D-635).

ومن خلال نتائج القياسات أعلاه تبين بأن للمضافات المشار اليها في أعلاه ، فعالية كبيرة في تثبيط لهوبية وزيادة مقاومة اشتعال راتنج البولي استر غير المشبع وراتنج الايبوكسي. وكانت كفاءة المضافات وفقاً للترتيب الآتي:

A10 > A4 > A8 > A3 > A7 > A6 > A5 > A2 > A1 > A9

حيث أظهرت الدراسة ، انه تم الحصول على إعاقة جيدة للهب في كل النسب المئوية للمضافات والحصول على إطفاء ذاتي في النسبة 0.2 % لكل من المضاف A4 و المضاف A10 ، وحصول إطفاء ذاتي في النسب 0.4 % للمضاف A3 و المضاف A10 ، كذلك فقد تم الحصول على عدم اشتعال للشريحة البوليمرية (Non-Burning) في النسب 0.4 % للمضاف A4 و المضاف A10 وكذلك في النسب 0.6 %للمضاف A8 لراتنج البولي استر و في النسبة 0.6 % للمضاف A4 و المضاف A10 لراتنج الأيبوكسي .