EPOXIDISED NATURAL RUBBER FOR AUGMENTED REINFORCEMENT OF SILICA FILLED NATURAL RUBBER

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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IN
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BY
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CERTIFICATE

Certified that this Project Report entitled " Epoxidised Natural Rubber For Augmented Reinforcement Of Silica Filled Natural Rubber " is the bonafide record of work done by MANJUSHA.K.S in a partial fulfillment of the requirements for the award of the degree of Master of Science in Applied Chemistry, Department of Chemistry, University of Calicut.

Guided by

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The Rubber Research Institute of India
Rubber Board, Ministry of Commerce and Industry, Govt. of India

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CERTIFICATE

This is to certify that the thesis titled " Epoxidised Natural Rubber For Augmented Reinforcement Of Silica Filled Natural Rubber " being submitted by Ms. Manjusha K. S. to the Department of Chemistry, University of Calicut, for the award of the Degree of Master of Science in Applied Chemistry is a record of bonafide research work carried out by her. Ms. Manjusha has worked on her research topic from March to June 2011, under my supervision. The results included in this report have not been submitted for the award of any other degree.

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Manjusha K.S.

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CHAPTER 1

INTRODUCTION

1. REINFORCEMENT OF RUBBER[1]

Basically reinforcement material means, a material that can impart extra strength to the original material. Reinforcement related to composite of two or more elements or component of different character there by strength of one of the element is imparted to the composites. Reinforcement with regard to polymer means imparting desired physical properties to the polymer usually with the incorporation of filler such as fibers, particle fillers etc. Mechanism responsible for the reinforcement of elastomers by particle filler means, it impart additional strength to the composite by maintaining its flexibility. The term reinforcement of rubber by filler, basically envisages the improvement of modulus and the other physical properties of rubber product.

1.1. Basic factors responsible for reinforcement[1]

Three important factors responsible for the particle reinforcement for rubber are particle size, surface area and specific surface activity/chemical composition.

1.1. a. Particle size

Fine particle fillers have a greater effect on reinforcement than coarse particle. The smaller the particle greater the extend interface between polymer and filler. Size and shape of the particles of the filler may be different in different filler. Particle size can be measured using electron microscope, sieve, light reflectance etc.

Primary properly a particulate filler must possess to reinforce rubber is the finer particle size. Tensile strength varies inversely with particle size

1.1. b. Surface area

Surface area is one of the most important filler properties. It is usually measured by gas absorption methods.

1.1. c. Specific surface activity

The nature of the filler surface may be varying in chemical sense having different chemical group. Some elastomers having group like polar nature will interact more strongly with such filler having –OH, -COOH, chlorine etc. Chemical group on surface of filler also play an important part on rate of cure with many vulcanizing system. Typical one such system is the use of carbon black or silica in rubber as a reinforcing agent.

1.2. CONDITION FOR REINFORCEMENT[2]

1. 2.1. Particle size influence

Primary property a particulate filler must possess to reinforce rubber is the finer particle size. Tensile strength varies inversely with particle size

1.2.2. Filler reinforcement factor

- Intensity – chemistry of surface
- Extensity - Chemistry of surface
- Geometric – shape and porosity of particle

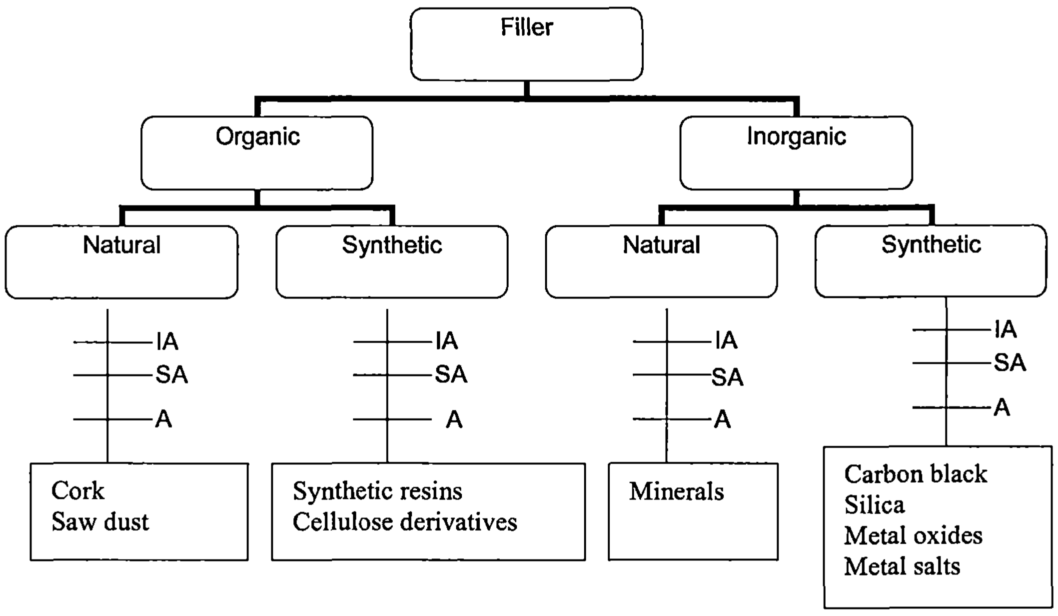
Reinforcing factor = total surface area x specific surface activity

Reinforcing filler is filler that improves the mechanical and physical properties (tensile strength, tear, and resilience and abrasion resistance) of the final vulcanization.

1.3. FILLER TYPE AND REINFORCEMENT[2]

Resins, fibers, particulate fillers etc. are the usual rubber reinforcing agents. The particulate fillers can be grouped according to their activity as inactive, semi active and active. Chart 1 gives the classification.

Chart 1



IA – Inactive, SA – Semi active, A - Active

Fillers are effective reinforcing agents. The surface activity of filler makes its surface function as radical acceptors, resulting in the formation of bound rubber, which also depends on filler loading[3]. The earliest tyres used Zinc oxide (ZnO) for reinforcement and were white[4]. Later carbon black and ZnO competed for the role of reinforcing agents. The potential of fine particle silica to reinforce elastomers to an extent comparable with the most efficient furnace black has been indicated by the extent and the nature of the bound rubber formation.

1.4. PARTICULATE FILLERS

Particulate fillers used in rubber industry in general can be classified as "Black" and "Non black", depending on their origin, the former being mostly produced from petroleum feed stock and the latter from mineral sources. The most important particulate fillers being used in rubber industry are carbon black and silica. Silicates, clays, whiting (calcium carbonate) and other mineral fillers are used extensively where a high degree of reinforcement is not essential [5].

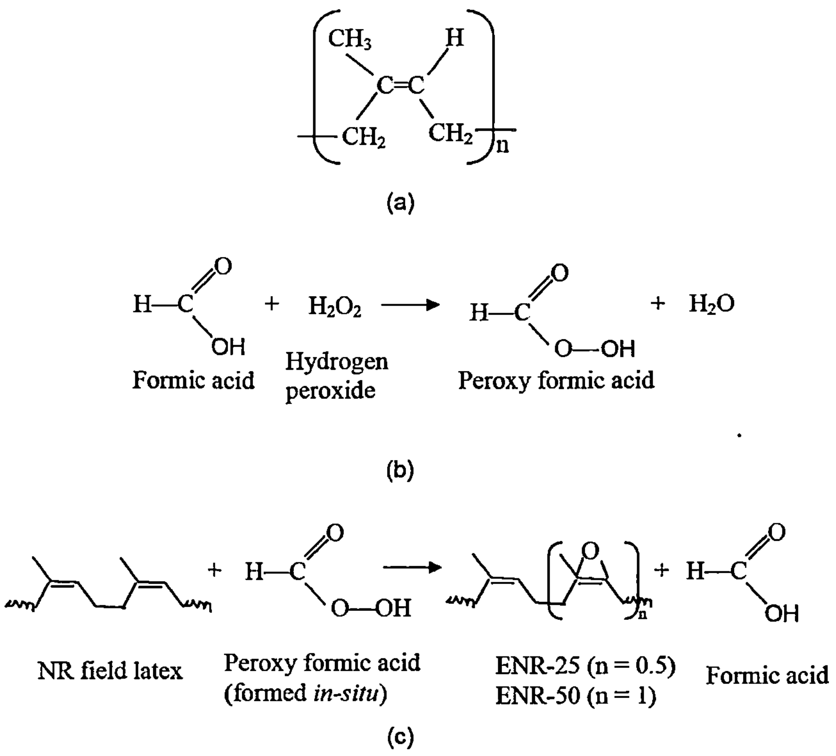
1.5. REINFORCEMENT OF NATURAL RUBBER

1.5.1. Natural Rubber[6]

Natural rubber is an important commercial raw material for the rubber industry. It is a high molecular weight polymer with visco-elastic properties. Structurally it is *cis* 1, 4 polyisoprene and is a diene. 1, 4 addition leave a double bond in each of the isoprene unit. Commercial production of the natural rubber is from the latex of '*Hevea Brasiliensis'*. At present annual production of natural rubber is about 10 million tones and about 4 to 5 million tons is consumed by the tyre industry alone[7]. Product made from natural rubber may be reinforced or non-reinforced. Product such as gloves, latex threads etc are generally non-reinforced. Majority of the product made out of natural rubber are reinforced. Major reinforcing fillers being used are *carbon black* and *silica*. The major properties with regard to products such as tyres are its wear resistance, flex resistance, environment resistance, heat resistance etc. The heat generated in the tyre of a vehicle can adversely affects its life and also results in the wastage of fuel equivalent to the energy lost in the form of heat. Optimization of the properties in a tyre compound hence is very significant.

1.5.2. Epoxidised Natural Rubber [8-10]

A relatively new modification of NR produced in commercial quantities is epoxidised natural rubber. The systematic study of the epoxidation of natural rubber with peroxy acid acetic acid revealed that high total acid concentration and elevated temperature favored the formation of secondary ring products. Gelling et.al later optimized the conditions for the preparation of ENR with different levels of epoxidation and to avoid ring opened products. ENR is industrially produced through the latex stage epoxidation of natural rubber using performic acid generated *in situ* from formic acid–hydrogen peroxide combination. Epoxidation of natural rubber is stereo specific and is as 1, 4- poly isoprene with epoxide ring randomly distributed along the polymer back bone. Different levels of epoxidation could be achieved by varying the concentration of reactants. A reaction mechanism for the preparation of ENR is given below.



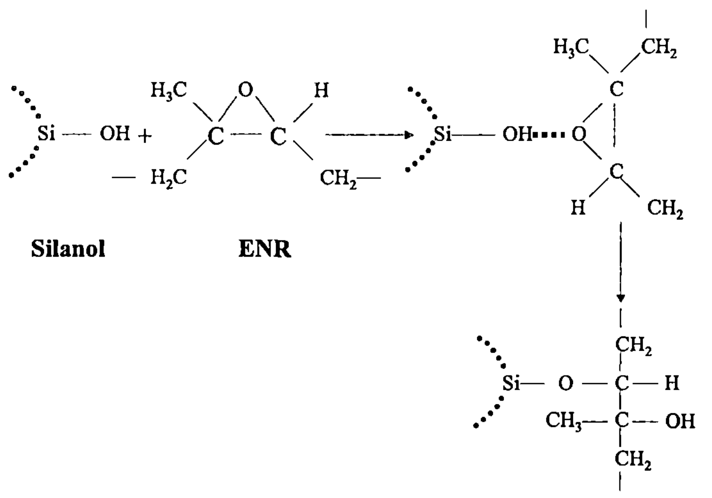
(a) Structure of natural rubber, cis-1, 4-polyisoprene, (b) formation of peroxy formic acid and (c) the production of ENR

The conventional designations used for 25 and 50 mole % epoxidation are ENR -25 and ENR 50.

Advantages of ENR over NR are

1. Improved oil resistance
2. Low gas permeability
3. Because of the polarity induced by epoxidation these rubbers are used in adhesives

ENR also shows good interaction with silica through epoxy-silanol interaction[11] as given under.



1.5.3. Carbon black[5]

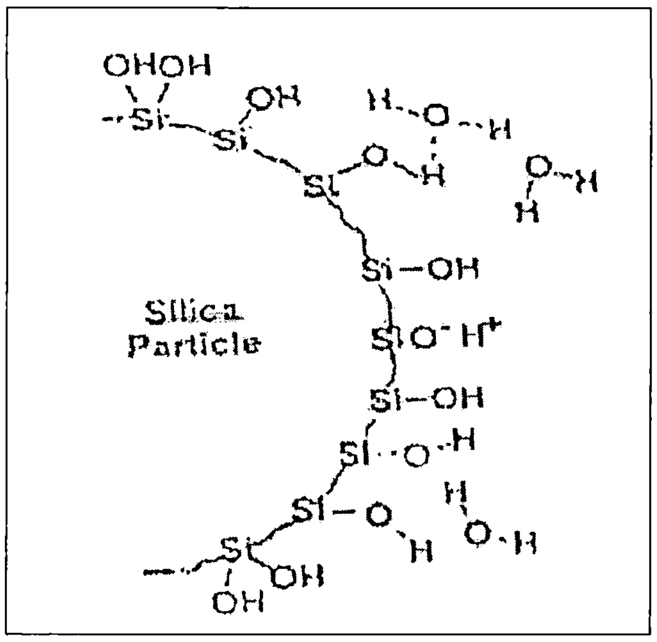
Carbon black is the most important particulate filler used in the rubber industry. It is a product made out of petroleum derivatives. Carbon blacks are prepared by incomplete combustion of hydrocarbons or by thermal cracking. Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black depending on their method of manufacture. The major types of rubber reinforcing carbon blacks are manufactured by the furnace process. The predominant purpose of furnace type carbon blacks in elastomers is the reinforcement they impart to the vulcanizates [12-14].

All carbon blacks have chemisorbed oxygen complexes (i.e., carboxylic, quinonic, lactonic, phenolic groups and others) on their surfaces to varying degrees depending on the conditions of manufacture. Different functional groups are formed on the surface of Carbon Black Pigments during production and also during subsequent oxidation processes. These surface groups increase the polarity of the surface area and as a result, they influence the properties such as rheology, wettability, etc.

Petroleum sources are fast getting depleted. Hence mineral filler such as silica will be a better option in tire compounds than carbon black on ecological grounds.

1.5.4. Silica[5,15]

Amorphous silica consists of ultimate particle of the inorganic polymer (SiO_2), where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atom. Each of the four oxygen atom is covalently bonded to at least one atom to form either a siloxane (-Si-o-Si-) or a silanol (-Si-O-H) functionality. Particulate silicas are made by precipitation from aqueous solution. The physical and chemical properties of precipitated silicas can vary with manufacturing process. The surface area, as determined by adsorption, is a function of the ultimate particle size. Ultimate particles can range from 5 to 50 nm in diameter. Aggregates are three-dimension clusters of ultimate particle covalently bonded to one another via siloxane bonds, and range in size up to 500nm in diameter. Because of its small particle size and complex aggregate structure, precipitated silica imparts the highest degree of reinforcement to elastomer compound among all of the non-black particulate filler. Precipitated silica is used to improve the tear strength, resistance to flex fatigue (cracking, cut- growth) and heat ageing of wide variety of manufactured rubber goods. Characteristic chemical groups on the surface of these fillers play an important role in reinforcement. Silica surface contain hydroxyl groups on its surface. Typical silica surface groups are shown below.



Adsorptive nature of silica filler

1.5.5. Difficulties in mixing silica and rubber[16]

Because of small size and large specific surface area, the incorporation of silica in to rubbers by the usual mechanical mixing techniques causes few difficulties such as high viscosity build up. Silica can also deactivate commonly used curing agents and accelerators and basic difficulty lies in the incompatibility between inorganic silica and organic rubbers. This causes aggregation of silica particles in the rubber matrix which often results in poor dispersion of silica particles

1.5. 6. Use of silane coupling agent in rubber/silica system [15]

To increase the compatibility between the organic silica and natural rubber, silane coupling agents are used. Coupling agents are designed to increase the interaction between filler and rubber to produce better dispersion of filler in the rubber. Thus the aggregation that may be formed due filler-filler interaction can be lowered by the use of coupling agents.

Both surface morphology and surface chemistry play an important role in the interaction of filler with coupling agent. For example, the dipole-induced dipole interaction between polar groups, such as siloxane and silanol, on the surface of silica with non-polar group of hydrocarbon elastomers are weak compared to the dipole-dipole interaction resulting from the hydrogen bonding between surface silanol groups in silica aggregates

The main functions of coupling agent are

(1) To modify the filler surface to reduce the filler-filler interaction.

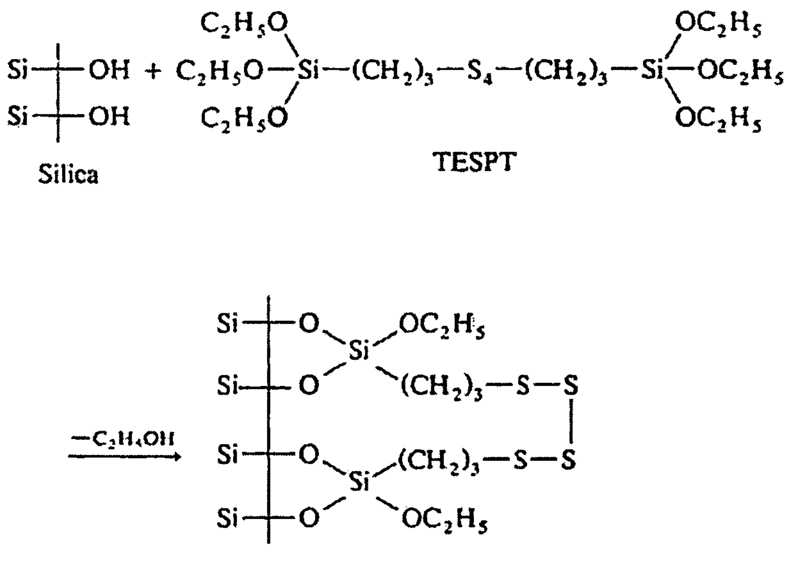
(2) Introducing covalent bonds between filler surface and polymer chain to strength polymer-filler interaction.

(3) Generating high bound-rubber content to prevent the filler flocculation.

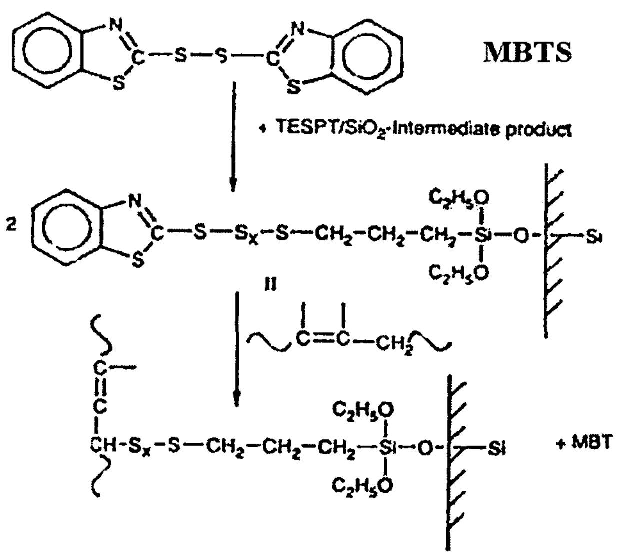
(4) To modify filler surface to improve wetting and dispersion and reduce the tendency to tie up ingredients of cure system.

Silanes generally used for surface treatment of mineral fillers are of three categories, Viz; Monofunctional silanes, bifunctional silanes and non-sulphur bearing silanes. Bifunctional silanes are commercially used by the rubber industry for improving the rubber-silica interaction.

Bis (triethoxy silyl propyl) tetrasulphide (TESPT) is unique and quite important in the rubber industry especially tire industry. The use of silane coupling agent has enabled silica, to be used extensively in auto mobile sector to manufacture non-back tires. A typical mechanism of reaction between silica, silane (TESPT) and rubber is given below.



Silica/TESPT intermediate product



Schematic mechanism of reaction between TESPT silane coupling agent silica and rubber

Although it is generally difficult to disperse hydrophilic silica in hydrophobic rubber, TESPT bond to silica in hydrophobic silica surface by alkoxylation at the mixing stage. Rendering the surface hydrophobic and hence facilitating dispersion, the tetra sulphide segment is believed to bond chemically to the rubber at the vulcanization stage.

1.6. VULCANIZATION OF RUBBER[1,15]

Vulcanization is chemical process designed to reduce the effect of heat, cold or solvents on the properties of rubber compound and create useful mechanical properties. This is most often accomplished by heating with vulcanizing agents such as elemental sulphur, organic peroxides, organic resins, metal oxides or urethanes with different rubbers. Most common industrially used vulcanizing agent for conventional rubbers is sulphur.

1.6.1. Vulcanizing agent

Sulfur is the most widely used vulcanizing agent in conjunction with activators (metal oxides and fatty acids) and organic accelerators. These are primarily used with general purpose rubbers such as natural rubber (NR), styrene butadiene rubber (SBR), polybutadiene rubber (BR), epoxidised natural rubber etc as all of these contain unsaturation(double bonds). Sulphur used in rubber industry is a yellow power of 99.0-99.8% purity. In natural rubber 1.6% of sulphur can be dissolved at room temperature and its solubility increases with increase in temperature. The advantages of using sulphur as a vulcanizing agent are,

1. It prevent the blooming of sulphur on to the surface of vulcanizate
2. It doesn't decrease its building tack
3. It doesn't pass from one level to the other in assembled products
4. It doesn't reduce the scorch safety of stored compound

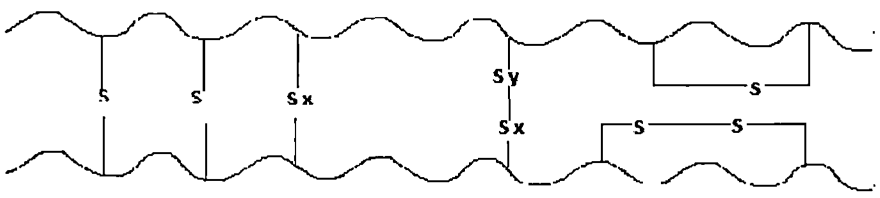
1.6.2. Mechanism of vulcanization using sulphur [1,17]

The initial step in vulcanization is the reaction of sulphur with the zinc perthiosalt Xsx ZnSxX, where X is a group derived from the accelerator (eg. thio carbamate or benzthiazyl groups). This salt reacts with the rubber hydrocarbon RH to give a rubber bound intermediate.

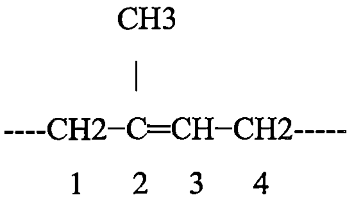
$$X\,S_xZn\,S_xX \; + \; RH \rightarrow X\,S_x\,R \; + \; ZnS \; + \; HS_{x-1}X$$

And a perthio-accelerator group which with further ZnO will form a zinc perthio-salt of lower sulphur content this may again be an active sulphurating agent forming intermediates Xsx-1R. The hydrogen atom which is removed is likely to be attached to a methylene group in the X-position to the double bond, i.e., in natural rubber the hydrogen atoms at positions 4 and 5 the most liable in this type of reaction.

In general, sulphur vulcanization shown as follows



And a perthio-accelerator group which with further ZnO will form a zinc perthio-salt of lower sulphur content this may again be an active sulphurating agent forming intermediates Xsx-1R. The hydrogen atom which is removed is likely to be attached to a methylene group in the X-position to the double bond, i.e., in natural rubber the hydrogen atoms at positions 4 and 5 the most liable in this type of reaction.

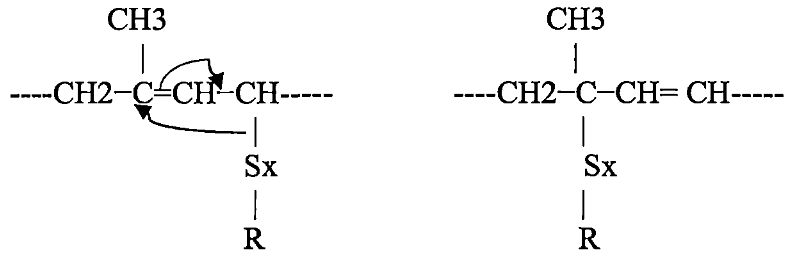


$$\begin{array}{c}CH3\\ |\\ ----CH2-C{=}CH-CH2-----\\ \;\;1\quad 2\quad 3\quad 4\end{array}$$

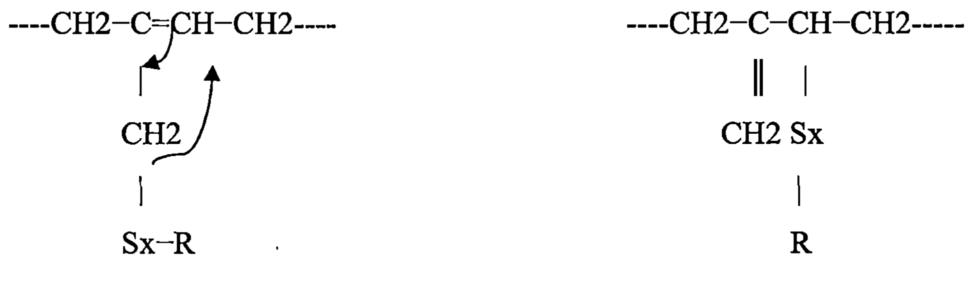
The intermediate XSxR then react with a molecule of rubber hydrocarbons RH to give a crosslink and more accelerators is regenerated.

$$XS_xR \;+\; RH \longrightarrow RSx\text{-}1R \;+\; XSH$$

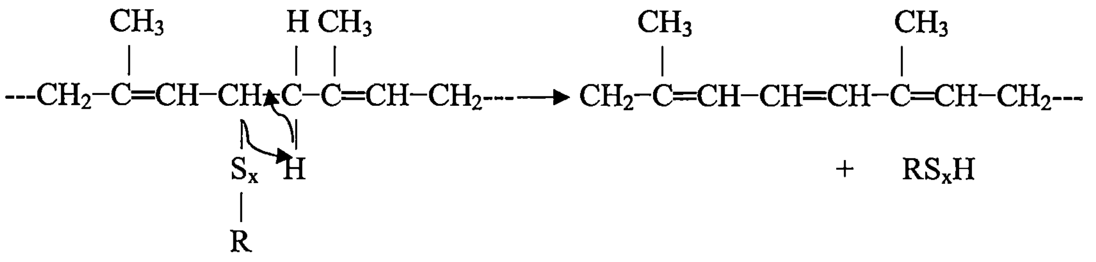
It is evident that the cross links which were initially at positions 4 and 5 undergo an allylic shift, with the result that new configuration appear.



And



At the same time, disappearance of crosslinks of the disulphide and polysulphide type occurs with formations of conjugated trienes.



$$\text{---}CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\underset{R}{|}}{\underset{S_x}{CH}}-\overset{H}{\overset{|}{\underset{H}{C}}}-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\text{---}\longrightarrow CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH=CH-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\text{---} + RS_xH$$

A consideration of above reaction leads to the conclusion that, if proceeds as in the case of the final network will be highly cross linked with mainly monosulphidic bonds, and there will be relatively few modifications of the cyclic sulphide or conjugated such a network is termed efficiently cross linked.

1.6.3. Activators (ZnO and stearic acid)

For vulcanization by sulfur the most common activator used is zinc oxide and it is able to increase the cross linking efficiency. ZnO is a white powder with density 5570 kg.m^{-3}.

As an activator of vulcanization, zinc oxide requires the presence of sufficient amount of fatty acids which convert it in to a rubber soluble form. Natural rubber also already contains a certain amount of that acid (as a component of the so called acetone extract) and it is usually insufficient. Therefore their content adjusted to the required level by the addition of commercial stearic acid.

Zinc oxide react with stearic acids to form zinc stearate, which is soluble in the rubber and this facilitates the cross linking reactions. Usually curing of rubber is very slow. On adding ZnO and stearic acid, the rate is improved.

1.6.4. Vulcanization accelerators

Higher cross linking efficiency could be achieved by the use of activators and accelerators in a vulcanization process with sulfur. The accelerator has the following effect on vulcanization.

(1) Increase the vulcanization rate substantially.

(2) Increase the cross-linking efficiency of the vulcanization in presence of zinc activators.

(3) Diminish the modification of rubber hydrocarbon then improving the resistance of vulcanizate to ageing.

(4) Permit the adjustment of the vulcanization system according to technological requirements and simultaneously according to the physical properties of the vulcanizate required.

Functionally, accelerators are typically classified as primary or secondary. Primary accelerators usually provide considerable scorch delay, medium to fast cure and good modulus development. Secondary accelerators usually produce scorchy, very fast curing stocks.

Important primary accelerators are thiazoles and sulfenamides. The sulphenamides are reaction products from MBT or MBTS (Mercaptobenzothiazole or the disulphide of MBT) and the amines. Examples of commercial sulphenamides are cyclohexyl benzthiazole sulphenamide (CBS), tertiary butyl benzthiazyl sulphenamide (TBBS) etc.

Important secondary accelerators are diphenyl guanidine (DPG), tetramethyl thiuram disulphide (TMTD) etc. The secondary accelerators are seldom used alone, but generally are found in combination with primary accelerators to gain faster cures.

1.7. PROCESS OIL [15]

Oils are generally added to the polymer itself during manufacture or to the rubber compound. In the first it is called as extender oil and in second case is called as process oils. Process oils when added to the rubber compound at 5 to 20 phr are considered to be process aids. Oils are added either to the polymer or to rubber compounds primarily to lower viscosity and to reduce both the stress/strain resistance and the hardness of the finished product. Fillers in general increase the viscosity whereas process oils reduce the viscosity. The three principal type of rubber process oils are aromatics, naphthenic and paraffinic. Naphthenic oil is more compatible with natural rubber.

1.8. ANTI OXIDANT [15]

As most of the rubber products are susceptible to oxidative degradation especially under dynamic condition, anti oxidants are also added in the rubber compound to protect the product from immature failure.

1.9. OBJECTIVE OF THE PRESENT WORK

Silica filled natural rubber is widely used in many type of rubber products such as tyres especially bus, truck and in off the road tyres. Conventionally carbon black is used as filler in such tyres. Carbon black since is a petroleum based product is not considered as an eco friendly material. Attempts are being made to replace carbon black with silica in rubber products especially in tyres. Silica as a filler in products such as tyres has high significance as it is more eco friendly than carbon black on two grounds Viz; as it has its origin from mineral sources and also contributes to lower rolling resistance in tyres resulting in lesser fuel consumption in automobiles.

As natural rubber being a hydrocarbon rubber and silica being polar filler, silica dispersion will be poor in natural rubber. To achieve optimum reinforcement with silica in hydrocarbon rubbers, its dispersion in rubber is to be improved. In order to improve the rubber-filler interaction, silane coupling agents are generally used. The present study is an attempt to augment the silica reinforcement of natural rubber both with silane and epoxidised natural rubber.

CHAPTER 2

EXPERIMENTAL

The details of the material used and the experimental techniques adopted in the present investigation are described in this chapter.

2.1. MATERIALS USED

2.1.1. Rubber

2.1.1.1. Natural rubber [18,19]

The natural rubber (NR) used was the technically specified rubber as obtained from the Rubber Research Institute of India, Kottayam. This rubber conforms to the Bureau of Indian slandered (BIS) specification for ISNR-5 grade natural rubber. The BIS specifications for ISNR-5 are given in **Table1.** The rubber was also characterized using FTIR (Fourier Transform Infrared spectroscopy, using the equipment *PERKIN ELMER, spectrum BX or model* 1600. IR spectrum of natural rubber is given in **Figure 1.** Characteristic peak for natural rubber is at 837 cm^{-1} which corresponds to the C-H deformation peak of cis - C= C –H .

Table 1. Specification of ISNR-5 grade natural-rubber

Parameter	limit
Dirt content %(max)	0.05
Volatile mater % (max)	1.0
Nitrogen content % (max)	0.7
Ash content % (max)	0.6
Initial plasticity %(max)	30.0
Plasticity Retention Index	60.0

2.1.1.2. Epoxidised natural rubber [8, 19]

Natural rubber epoxidised to varying levels of epoxidation (10 , 17.5, 25 and 50 %) were used for the work. Epoxidised natural rubber **(ENR)** was prepared from centrifuged natural rubber latex using performic acid generated *in situ.* By suitably adjusting the concentration of reactants, the level of epoxidation was varied. When NR was epoxidised to different levels of epoxide content, the characteristic IR peak of NR at 837 cm-1 get diminished and a new peak at 872 cm-1 appears. From the intensity of these two peaks the level of epoxidation was calculated. IR graphs obtained for ENR 10, 17.5, 25 and 50 are given in **Figures 2,3,4 and 5**. When NR is epoxidised, some of its properties such as air permeability, oil resistance and silica affinity are changed. As the ENR is having better affinity for silica, in the present experiment ENR of different levels of epoxidation was blended with NR to improve its silica reinforcement.

2.1.2. Filler

2.1.2.1. Silica[20]

The reinforcing filler used for the experiment is Ultrasil VN3 type silica a product of Degauss a A.G, Germany. It is having specific surface area 175 m2/g, tapped density of 220 g/l, SiO_2 content of 98 % , moisture content of about 5.5% by weight and pH of 6.2.

2.1.2.2. Carbon black

In the present experiment ISAF black was used as filler. Typical properties are given below

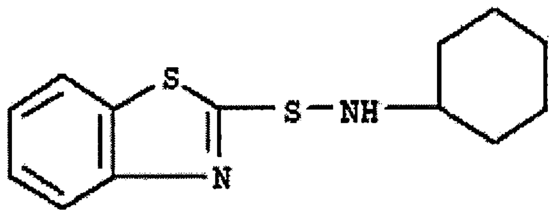
Black		Name	Surface area (m^2/g)	Average particle size (nm)	DBP absorption (cm^3/g)
ASTM	Type				
N220	ISAF	Intermediate super abrasion furnace	120	24-33	1.14

2.1.3. Vulcanization accelerators

Higher cross linking efficiency could be achieved by the use of activators and accelerators in a vulcanization process with sulfur. The accelerator has the following effect on vulcanization.

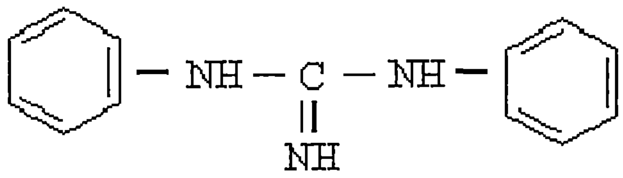
In this experiment two type of accelerators were used viz; N- cyclohexyl banzothiazole-2-sulphenamide (CBS) and N, N Biphenyl guanidine (DPG). In carbon black filled system usually primary accelerator alone is used. In the present study CBS was used as the accelerator. In silica filled systems a combination of CBS and DPG is used as silica surface may adsorb a part of the accelerator.

CBS is a yellowish powder with a faint smell, soluble in acetone, benzene, ethanol, chloroform etc. Owing to its low melting point it is very well dispersed in rubber. It is a fast and high modulus accelerator with a delayed action. During the processing it is safe at temperature 135°C and it is very active.



N-Cyclohexyl-2-benzothiazole sulfenamide

DPG is a white grayish powder soluble in acetone, benzene, ethanol etc. readily dispersible in rubber having good storage ability. It is used as a secondary accelerator for vulcanization of silica filled rubbers.



DPG

2.1.4. Antioxidant

In the present experiment [N-(1, 3 dimethyl butyl) -N' Phenyl –p-phenylene diamine] a Merchem product under the trade name Mernox *6C* was used as an antioxidant.

2.1.5. Coupling agent

Two coupling are most frequently used in silica compounding viz. mercapto-propyl trimethoxy saline and *bis* [3-tri methoxy –silylpropyl] tetra sulfate. Latter is used for the present experiment. The material used is SI-69, a 'Degussa' product.

2.1.6. Process oil

Naphthenic oil was used as process oil

2.2. RAW RUBBER CHARACTERIZATION

2.2.1. Equipments

2.2.1.1. Mooney viscometer[23]

Mooney viscometer used for the experiment was of 'Rheo Technologies' Model No. MV 2000. The viscometer consists of a rotor head and a hollow cylindrical two pat die, serrated or their complimentary surface by grooves. The rotor head is mounted. The dies are heated at a specified temperature within ±0.5°C. Rotor is rotated by means of a motor at a speed of 2 ± 0.2 revolutions per minute. The viscometer plates are closed or opened by a suitable device. A gauge is provided for indicating the torque applied to the rotor.

The die cavity and rotor are heated to test temperature i.e. 100°C and allowed to reach steady state. The die cavity is opened, the rotor with the test sample is placed in the die cavity and it is closed. The pressure is maintained within 1150±50 psi. One minute after closure of die, the rotor is started and reading taken. Normally for large rotor, reading at the 4th minute from the start of rotor is taken as the Mooney viscosity and the result is expressed as ML (1+ 4) at 100°C, where M denoted viscosity in Mooney, L- large rotor, 1-preheat time(minutes), 4-time (minutes) when the reading after preheating was taken.

The Mooney viscosity values determined for NR and ENR of different epoxy content are given in Table 1.

Table 1 – Mooney viscosity of raw rubber

Raw rubber sample	Mooney viscosity, Ml(1+4) 100°C
Natural rubber	70
ENR 10	90
ENR 17.5	121
ENR 25	124
ENR 50	140

Before compounding, the rubber/ rubber blend was masticated to uniform viscosity in the mixing mill and then compounded in the internal mixer

2.3. COMPOUNDING AND MOULDING MACHINERY

2.3.1. Compounding machinery

2.3.1.1. Internal mixer[21]

An internal mixer comprises two parallel kneading rotors, each rotating within the corresponding region of a double trough. The upper central region of the mixing chamber is constituted by a ram or floating weight which is V shaped at the bottom. Discharge is through the bottom which is an inverted V section in the form of a hanged 'drop door' operating hydraulically. The ram can be lowered or raised within a hollow vertical shaft, hydraulically, thus providing a chaining entry when in raised position and sealing the mixing chamber when lowered. Capacity of the mixer is one liter. Mixing was done at 85 % volume loading.

2.3.1.2. Two roll open mixing mill[22]

The two roll mixing mill consists of two rolls, revolving at different speeds and in opposite directions. The back roll is driven from the gearbox or back shaft and the front roll through roll and gears. The rolls are made of chilled cast steel, cored to allow circulation of water for efficient cooling. Another important feature of the mill is the friction ratio. i.e., the relative surface speed at which the two rolls revolve. The ratio depends upon the size of the mixing mill.

2.3.1.3. Preparation of compounds

The rubber used for compound preparation was physically characterized for its Mooney viscosity using Mooney viscometer.

2.3.1.4. Mastication / blending

Natural rubber and epoxidised natural rubber used for the experiment was in the high viscosity range as indicated by the Mooney viscosity values in Table 1. Initial mastication/blending of the raw rubber/ rubbers to a Mooney viscosity of 60±3 was done in the two-roll mixing mill operated at a friction ratio of 1:1.25.

2.3.1.5. Compounding

The formulations of the mixes prepared for evaluation under the present study are given in Table 2.

Table2 Formulation of mixes

Ingredients	Compound number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
NR (ISNR 5)	100	100	85	85	85	85	85	85	85	85	100	85	85
ENR 10	-	-	15	15	-	-	-	-	-	-	-	15	15
ENR 17.5	-	-	-	-	15	15	-	-		-	-	-	-
ENR 25	-	-	-	-	-	-	15	15	-	-	-	-	-
ENR 50	-	-	-	-	-	-	-	-	15	15	-	-	-
Silica	50	50	50	50	50	50	50	50	50	50	-	50	50
Carbon black	-	-	-	-	-	-	-	-	-	-	50	-	-
Silane	-	4	-	4	-	4	-	4	-	4	-	4	-
Naphthenic oil	5	5	5	5	5	5	5	5	5	5	5	5	5
Zinc Oxide	4	4	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
Anti oxidant[1]	2	2	2	2	2	2	2	2	2	2	2	2	2
CBS[2]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DPG[3]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	-	-	-
MBTS[4]	-	-	-	-	-	-	-	-	-	-	1.5	1.5	1.5
Sulphur	2	2	2	2	2	2	2	2	2	2	2	2	2

1. Mernox 6C, **2.** N-cyclohexyl benzothiazole-2-sulphenamide **3.** N,N biphenyl guanidine

4. 2-Mercaptobenzothiazole

Mixing of the rubber compounds was done in the Laboratory model internal mixer K0, MK3 of Francis Shaw, Manchester, England. Rotor speed, mixing time and temperature were controlled during mixing. Compounding of mixes was also done in the internal mixer. Mixing of each compound was done in three stages. Mixing sequence is given in **Table 3 a, b and c.** First stage mixing was done at 65 rpm, with initial temperature of 85 °C and the final temperature developed at the end of mixing is given in Table 4. For silane modified systems higher temperature is needed for achieving silica-silane reaction which is required for reducing filler-filler interaction. Second and third stage mixing also was done in the internal mixer with the initial chamber temperature set at 40°C and the rotor speed at 60 rpm.

The batch coming out from the internal mixer after first and second stage mixing was sheeted in the mixing mill. After the third stage of mixing the compound was finally homogenized in the mixing mill. The final dump temperature for the first stage of mixing is important as the reaction between silane and silica take place at high temperature. The compound after the third stage of mixing after homogenization was stored at a temperature of 25± 1°C for further processing.

Table 3 (a)

Stage 1	
Ingredients	Time (Sec)
Rubber	0
1/3filler+1/3oil+1/3silane	30
1/3filler+1/3oil+1/3silane	120
1/3filler+1/3oil+1/3silane	210
Dump	360

Table 3 (b)

Stage 2	
Ingredients	Time (Sec)
Master batch	0
ZnO + stearic acid	30
Antioxidant	120
Dump	210

Table 3(c)

Stage 3	
Ingredients	Time (Sec)
Master batch	0
CBS+DPG\MBTS+SULFUR	30
Dump	180

Table 4. Temperature development for stage 1 mixing.

Temp. Stage1	Compound number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Initial,	85	85	85	85	85	85	85	85	85	85	85	85	85
Final,	135	138	133	148	131	147	143	145	142	150	95	135	142

2.4. COMPOUND TESTING EQUIPMENTS

2.4.1. Moving Die Rheometer MDR 2000 [24]

The equipment used for measuring cure time was, **Moving Die Rheometer MDR 2000 of Alpha Technologies, USA.** The MDR 2000 Moving Die Rheometer is a curemeter designed to test rubber compounds under isothermal test conditions with constant strain and frequency and conforms to ASTM D 5289/ ISO 6502. The instrument could be operated under the following conditions.

Temperature: Ambient to 200 °C

Oscillation frequency: 1.667 Hz

Strain: 0.2, 0.5, 1.0 or 3.0 degree

Tests: Measures cure properties under isothermal test conditions at constant strain and frequency. Output dynamic properties during cure: S" and Tanδ

Equipment consists of two die cavities which can be electrically heated to the cure temperature (150° C). Lower die oscillates at the set frequency and strain (0.5 degree). Compound to be tested is placed in the lower die cavity and the platens are closed with set pressure. As the compound get cured reaction torque experienced by the upper die is sensed and measured using appropriate devices. A plot of cure time versus cure torque is generated. From the graph M_L (minimum torque), M_H(maximum torque), Ts_2 (time for two units torque rise), T_{90}(time for 90 % cure), T_{95}(time for 95 % cure) were calculated.

Cure rate index (CRI) is calculated using the following equation.

$$\mathrm{CRI} = \frac{\mathbf{100}}{\mathbf{T_{90}-t_{s2}}} \qquad \text{-------------} \ (1)$$

Copy of the rheographs are given in Figures 6 -18(corresponding to compounds 1 to 13) Rheometric values are given in **Table 5**

2.5. MOULDING OF TEST SAMPLES

2.5.1. Moulding machinery

2.5.1.1. Hydraulic press[22]

The press shall be capable of exerting a pressure of not less than 3.5 MPa (500 psi) on the total cross sectional area of the cavities of the mold during the entire period of vulcanization. There are two heated plates. The lower platen moves under hydraulic pressure. Molding operations include cleaning the mold surfaces, preheating the mold initially to curing temperature, application of mold releasing agent, loading of the compound, pressure application, curing and stripping. Hydraulic press used for the present experiment was **Fontune presses manufactured by M/s fontijne, Netherland, Model no .TP.600**

The sheeted out compounds were compression moulded using the hydraulic press at 150°C and the molding pressure was 1600 psi. These compounds were cured to its optimum cure time. Test samples for Tensile/Tear properties, Compression set, Heat build up, Resilience, Demattia flexing, DIN Abrasion loss were moulded as per the respective ASTM standards.

2.6. PHYSICAL TEST METHODS

For parameters described below, respective ASTM/DIN/BS/ISO standards were followed.

2.6.1. Modulus, tensile strength and elongation at break [25]

Vulcanized sheets of samples were prepared from the thirteen test compounds as per ASTM D 412.

Tensile properties were determined according to the ASTM 412-80 test method, using dumb-bell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die, along the mill grain direction of the vulcanized sheets. The thickness of the narrow portion of the specimen was measured using a dial gauge. The tests were carried out in a *Zwick Universal Testing Machine* (UTM) model 1474 at (25 ±2) °C and a cross head speed of 500 mm per minute. The modulus at 100, 200 and 300% elongation and tensile strength were recorded. Ultimate tensile strength and ultimate elongation result from pulling dumbbell specimen to rupture. The results are given in **Table.**6

2.6.2. Tear resistance [26]

The tear resistance of the sample was tested as per ASTM D- 624 test method, using un-nicked 90^0 angle test specimen. Samples were punched out from the sheets parallel to the grain direction. This test was also carried out Using the 'Zwick UTM'. The test sample was mounted on the testing machine. Steadily increasing force was applied at 500 ± 50 mm/min and at (25 ±2) °C until the test piece was completely ruptured. The tear strength values are reported in N/mm.

2.6.3. Hardness[27]

The hardness of the samples were measured as per ASTM D-2240 standards using a shore A type Durometer, which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indenter and the sample, the readings were taken immediately after the establishment of firm contact.

2.6.4. Abrasion resistance[28]

Abrasion resistances of the samples were measured using a DIN abrader (As per DIN 53516). It consists of a drum on to which a standard abrasion paper is fixed. The drum rotated at a speed of 40 ±1 rpm and the total abrasion length is 42 m. Sample having a diameter of 16 ±0.2 mm and thickness of 6-10 mm is kept on rotating sample with a 10 N load applied over the sample. Initially a pre-run was given for the test sample for a definite distance and it was weighed. The weight after the final run was also noted. The difference in the weight is the abrasion loss. It is expressed as the volume of test piece getting abraded away by its travel through 42 meters on a standard abrasive surface. The abrasion loss is calculated as follows.

$$V = \frac{\Delta W}{\rho} \times 1000 \quad \text{------------------} \quad (2)$$

Where

ΔW is the weight loss, ρ - specific gravity and V - abrasion loss.

2.6.5. Compression set [29]

The test was done as per ASTM D-395. The samples were compressed in the compression set apparatus to give 25 per cent compression. It was then kept in air oven at 70^{0}C for 22 hours. After the heating period, the samples were removed, cooled to 28 ± 1^0 C for half an hour and final thickness was noted. The compression set was calculated as follows.

$$\text{Compression set (\%)} = \frac{(t_0 - t_1)}{(t_0 - t_s)} \times 100 \quad \text{---------} \; (3)$$

Where' t_0' and t_1 are the initial and final thickness of the specimen. t_s IS the thickness of the space bar used.

2.6.7. Rebound resilience[30]

The test procedure followed in accordance with BS 903: part A8. The equipment used for the test was 'Dunlop Tripsometer', which consists of a pendulum made of solid steel disc of 41.9 ±0.13 cm in diameter. The disc carries a bracket which holds a steel ball 4 ±0.04 mm in diameter with its centre 20 ±0.05 cm from the centre of the disc, the ball and bracket together adding an unbalanced mass of 60±0.2g.

The sample was held in position by applying vacuum. Sample on the fixture was conditioning by striking with indentor six times. The temperature of the specimen holder and the sample was kept constant at 25 ±1^0 C. Rebound resilience was calculated as follows.

$$\text{Rebound resilience} = \frac{1 - \cos\theta_2}{1 - \cos\theta_1} \times 100 \quad \text{------------------} \; (4)$$

Where

θ_2 = Angle of rebound

θ_1 = Original angle, i.e., 45^o in all cases

2.6.8. Flex fatigue resistane[31]

The test was carried out as per ASTM D 430.

Rubber flex fatigue can be defined as deterioration in any physical property resulting from extended exposure to a cyclical deformation, such as occurring in bending, shearing, compression and extension.

There are two types of fatigue tests which measure quite different properties, the flex cracking test and heat –build up test.

2.6.8.1. Flex cracking test[31]

The test procedure followed was ASTM D 430. In this test, samples are fixed in a De Mattia flexing machine and are repeatedly bend in this machine. Sample is a moulded strip with a transverse groove. The test piece is bent by the two end clamps moving towards and away from each other, bending this test piece in a loop like pattern and placing a maximum strain at the surface in the groove. The heat from this type of deformation is dissipated and the specimen temperature stays close to ambient. There are two types of flex cracking characteristics, i.e. Cycles of test required for crack initiation and complete failure was noted.

2.6.8.2. Heat build-up test[32]

Test method followed was ASTM D 623. The equipment used was 'Goodrich Flexometer' This type of flex fatigue test is basically a heat build-up test, where the heat from flexing of cured specimens does not dissipate. In this test cylindrical rubber samples moulded as per the standard are mounted in a chamber in which the temperature is maintained at 50 ^{0} C. The temperature rise values were measured under repeated cylindrical compression of the sample. For the Goodrich flexometer, the length of the stroke, applied load, and base temperature can be set for the appropriate severity of test condition for the compound in question. Heat developed after twenty five minutes of flexing were measured.

The results of tear strength, hardness, abrasion loss, rebound resilience, compression set, demattia flexing and heat build up ae given in **Table 7.**

2.7. SPECIFIC TESTS FOR REINFORCEMENT CHARACTERISATION

2.7.1. Bound rubber content[33]

Bound rubber, sometimes known as filler gel, is an important factor in the mechanisms of rubber reinforcement and is also a measure of the surface activity. The filler-polymer interaction leading to the formation of bound rubber is influenced by factors like physicochemical character of filler and its morphology, the chemical as well as microstructure of the polymer molecules, processing conditions of the compound, such as mixing, storage times etc. and the nature of solvent and the temperature of the extraction.

For the measurement of bound rubber, the samples were conditioned at room temperature for 7 days. For the experiment, 0.2g of compound was cut in to small pieces and placed in a stainless steel wire mesh cage of known weight. The cage was then immersed in 25ml of toluene for 7 days at room temperature and the solvent was renewed after 3 days. After extraction, rubber and cage were dried for one day in air at room temperature and for 24 hr in an oven at 105^0C. The percent bound rubber of polymer, R_B was calculated as follows.

$$R_B = \frac{W_{fg} - W\,[m_f/\,(m_f + m_p)]}{W\,[m_p/\,(m_f + m_p)\,]} \times 100 \qquad \text{----------------} (5)$$

Where W_{fg} – weight of silica and gel
M_f – weight of filler in the compound
m_p – weight of polymer in the compound
W – Weight of specimen

Results are given in **Table. 8**

2.7.2 Determination of volume fraction- procedure[34]

Test pieces weighing about 0.2 g were punched out from vulcanized sheets of 2 mm thick and it was immersed in toluene taken in a squadish until it reached equilibrium. Test pieces were taken out from the solvent at definite intervals, loose liquid was rapidly removed by blotting with filter paper and the swollen weight measured repeatedly till it attained equilibrium. The test pieces were subsequently de-swollen in an oven at 70°C until it reached a constant weight.

The volume fraction of the polymer in the swollen sample was determined by using the equations reported by Ellis and Welding[34]

$$\text{Volume fraction} = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_0\,\rho_s^{-1}} \qquad \text{----------------- (6)}$$

where 'T' is the weight of the test specimen before swelling; 'D' the deswollen weight of test specimen; 'F' the weight fraction of the insoluble component vulcanizate; 'A_0' the weight of the absorbed solvent; ρ_r and ρ_s are densities of rubber and solvent respectively. (ρ_r = 0.92 and 0.94 g/cc for NR and ENR-50 respectively, ρ_s = 0.857 g/cc for toluene).

Results are given in **Table 9**.

CHAPTER 3

RESULTS AND DISCUSSION

Formulations of the rubber mixes studied are given in **Tables 2**. The compounds can be broadly classified into three groups viz. NR-silica, NR-silica composites modified with ENR and NR-silica composites modified with ENR and silane coupling agent. Compounds are numbered as 1 to13. In compounds 1 and 2 only NR was used. In compounds 3 and 4, NR and ENR-10, in compound 5 and 6 NR and ENR-17.5, in compound 7 and 8 NR and ENR 25, in compound 9 and 10 NR and ENR-50 were used. In all the formulations except 11, filler system used was silica. The filler used in the compound 11 was carbon black. For compounds 1 – 10, cure systems sulphur, CBS and DPG and in compounds 11- 13 sulphur, CBS and MBTS were used . Compounds were prepared in an Intermix. The mixing sequence is given in **Table 3a,b and c.**

3.1. MIXING

3.1.1. Mixing temperature

Mixing of compounds was done in the internal mixer in three stages. In the first stage of mixing for achieving high silica-silane interaction higher initial temperature and high shear rate was given. Required temperature range about 130 to 150 °C was achieved in the first stage (initial temperature 85 °C). Temperature developed during the first stage mixing of compounds 1 to 13 is given in **Table 4**. For the second stage of mixing temperature developed was in the range of 80 to 90 and for the third stage temperature developed was in the range of 60 to 70 °C (initial temperature 40 °C). First, second and third stage of mixing took 6, 3.5 and 3 minutes respectively.

3.2. COMPOUND CHARACTERIZATION

3.2.1. Bound rubber

Bound rubber values were calculated as per the Equation 5. It is a measure of the rubber-filler interaction in the compounded stage. Higher the bound rubber, higher will be the rubber-filler interaction. Observed bound rubber values are given in **Table 5.** The bound rubber can be affected by many factors like mixing conditions and dump temperature. In the present case some compounds showed high bound rubber values, while others gave erratic values. Compound number 2, 4, 6 and 13 gave comparatively higher bound rubber values which can be attributed to rubber-silane-silica interaction. Compound number 3,5,7 and 9 showed progressive increase in bound rubber which could be attributed to the higher epoxy content of the ENR and the corresponding enhanced bound rubber. Also compound 11, black filled compound and compound number 12 showed higher bound rubber values which could be attributed to higher rubber – filler interaction. Compound number 1 however showed higher bound rubber value which may be due to experimental error.

Table 5. Bound rubber content

No	1	2	3	4	5	6	7	8	9	10	11	12	13
Bound rubber content, (R_B),%	24.1	25.8	4.7	24.6	6.7	20.1	8.3	7.9	8.4	1.37	14.3	16.7	14.4

3.3. CURE CHARACTERISTICS

3.3.1. Rheometric values

Cure characteristics of the different compounds are given in **Table 6**. Among the thirteen compounds, NR-Silica compound (compound no. 1) exhibited the highest minimum torque value, which could be attributed to the higher filler-filler interaction. NR-silica-silane compound (compound no.2) exhibited lowest minimum torque value, which could be attributed to the reduction in filler-filler interaction. Minimum torque value observed for the ENR modified samples were lower than NR/Silica composites indicating lesser filler-filler interaction in these composites. These composites on further modification with silane reduced the minimum torque to a still lower value and was almost on par with that of carbon black filled system.The lower minimum torque values obtained for the compounds containing modifiers indicates lower filler-filler networking or in other words better processability. Maximum torque was highest with NR/Silica system and got reduced with ENR incorporation. With medium epoxy content and silane modification, the torque values and cure rate index were almost on par with that of carbon black filled. With ENR/silane combination cure time got considerably reduced. The optimum cure time was higher for the compound containing sulphur/CBS/MBTS systems.

Table 6. Rheometric values (MDR 2000)

Property	Compound number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Maximum torque, dN.M	30	18.56	26	23.2	22.62	24.5	25.52	25.23	28.42	20.3	23.2	21.46	22.62
Minimum torque,dN.M	6.47	0.87	3.48	1.16	2.32	1.16	2.61	1.45	4.06	1.16	1.74	3.48	1.16
Optimum cure, t_{90}, time(m:s)	8:58	6:03	10:05	4:34	9:40	4:47	8:31	4:08	9:05	5:24	7:51	13.08	10:40
Optimum cure, t_{95}, time(m:s)	10	7	11	5:30	10.45	5:45	9:30	5:15	10	6:30	8:75	14	12
Cure rate index ($100/t_{90}-t_2$)	5.59	7.45	6.54	5.44	7.26	5.55	6.01	4.92	5.58	6.46	5.92	7.96	7.07

3.4. TENSILE PROPERTIES

In cross-linked rubbers reinforcing fillers can enhance its mechanical properties viz. modulus, tensile strength etc. Tensile properties of the vulcanizates are given **Table 7**. It can be observed that the tensile strength values were almost closer in all the cases. The vulcanizate containing ENR showed higher modulus values over that of the unmodified. Samples containing both ENR and silane showed still higher modulus values and was even higher than that of carbon black. Silane modified NR/Silica composites showed modulus and elongation closer to that of carbon black filled. Systems modified with ENR alone showed elongation values in between that of NR/Silica and NR/Silica /Silane system. ENR and Silane modified system exhibited the lowest elongation. This indicates a better rubber-filler interaction in all the modified systems.

Table 7 .Tensile properties

Property	Compound number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Tensile strength, N/mm2	26.4	25.1	24.7	21.3	24	20.5	24.69	19.51	22.71	24.54	24.04	24.6	19.5
100% modulus, N/mm2	1.7	3.2	2.6	4.4	2.46	3.94	2.61	4.64	2.7	3.44	2.96	2.29	4.0
200% modulus, N/mm2	3.72	8.63	6.24	10.44	5.94	9.05	6.60	11.50	6.21	8.43	7.88	5.58	9.63
300% modulus, N/mm2	7.05	15.04	11.04	17.66	10.56	18.41	11.74	18.21	11.18	14.90	14.10	10.09	16.42
Elongation at break (%)	656.9	461.9	532	334	329	360	505	303	486	455.1	448.8	531.0	334.9

3.5. TECHNOLOGICAL PROPERTIES

Technological properties of the compounds are given In **Table 8**

3.5.1. Tear strength

The values of tear strength are given in the Table 8. In filled valcanizate, higher tear strength can be taken as a criterion of good reinforcement. In general NR/ENR/Silica composites showed higher value than NR/Silane/silica compound. ENR/Silane modification however showed lowest tear strength.

3.5.2. Hardness

Hardness values (Shore A) are given in Table 8. NR/ENR/Silica/Silane compound showed higher values of hardness even higher than carbon black filled NR and NR/Silane/Silica system. Hardness is also a measure of modulus, which in turn can be treated as a measure of reinforcement.

3.5.3. Rebound Resilience

A highly resilient material is the one which rebounds most of the energy expended when deforming it, and then springing back to its former shape. The values of the rebound resilience are given in the Table 8. Rebound resilience was found to be higher in NR/Silane/silica and NR/ENR/Silane/Silica compounds. Among these NR/Silane/silica and NR/ENR-10/Silane/Silica compounds showed higher rebound resilience values. ENR/Silane modified system exhibited higher rebound values than carbon black filled indicating lesser viscous component and higher elastic component. As the percent epoxy content increases rebound resilience also decreased.

3.5.4. Abrasion resistance

Results are given in Table 8. Silane modified systems gave the lowest abrasion loss or the highest abrasion resistance. NR/ENR-10/silica/silane gave comparatively better abrasion resistance than the carbon black filled compound. As the epoxidation level of ENR increased, the abrasion resistance decreased. Incorporation of ENR in NR/Silica system resulted in improvement of abrasion resistance.

3.5.5. Compression set

Compression set values are given in Table 8. NR/Silica/Silane system gave the lowest compression set (22.4 percent). NR/ENR /Silica system showed compression set values in a range from 26.8 to 43 % as the epoxy content increased from 10 to 50 per cent. from NR/ENR/Silica/Silane system showed lower compression set values in the range from 24.2 to 29.4 per cent. When the level of epoxidation of ENR increased compression set value in general increased. It must have resulted from the damping nature of ENR.

Table 8. Technological properties

Compound no	Properties						
	Tear Strength (kg/cm)	Hardness Shore A	Rebound Resilience (%)	Abrasion Loss, (mm^3)	Compression Set (%)	Demattia Flexing, Initiation/Failure	Heat Build Up(°C)
1	105.2	60	58.8	174	32.5	110119 /499285	15
2	90.8	62	70.9	109	22.4	11808 /625293	8
3	106.4	62	57.0	143	26.8	95005 /399466	15
4	53.4	67	70.2	96	27.9	110119 /310491	9
5	89.9	62	55.7	144	34.3	64527/243188	15
6	61.9	66	65.9	105	24.2	58120 /196058	9
7	97.9	63	52.5	149	37.2	25071/99301	16
8	53.7	68	63.8	104.7	29.4	39880 /196058	11
9	98.3	68	45.1	157	39.2	17105 /151395	19
10	89.1	64	53.8	114	28.9	97125 /307053	12
11	109	60	51.2	106.1	32.9	65057 /353364	19
12	77.7	64	58.3	146.4	43.0	36732 /372840	15
13	63.1	62	65.9	119.3	25.4	67424 /102588	9

3.5.6. Heat build-up

The values of heat build up are given in the Table 8. NR/Silica/Silane showed the lowest value (8 □ C). The values in general were lower for NR/ENR/Silica/Silane compound (varied from 9 to 12 □ C). The heat build up value increased with epoxidation level of ENR. This is due to the high clamping effect of ENR . Carbon black filled system showed highest heat build up.

3.5.7. Flexing

The values of DeMattia Flexing (initiation/failure) are given in the Table 8. NR/Silica with out any modification showed highest flex resistance. For NR/Silica system, though fast initiated it took more number of cycles for complete failure. On modification with ENR flex resistance in general showed decreasing trend and the failure cycles in general decreased with increasing epoxy content. However few ENR modified systems showed failure cycles comparable to that of carbon black filled.

3.6. REINFORCEMENT CHARACTERIZATION

3.6.1. Volume fraction (Vr) of rubber

Results of the study are given in Table 9. Higher the volume fraction of rubber (Vr) in a particular system higher will be the cross link density. On comparison of NR/Silica and NR/Silane/Silica the latter gave higher volume fraction of rubber indicating higher cross link density. ENR modified systems in general showed Vr values comparable to that of NR/Silica. However NR/ENR/Silica/Silane systems showed higher Vr values among all the samples studied and was even higher than carbon black filled system, which indicates higher cross link density in such systems.

Table 9. Volume fraction of rubber

No	1	2	3	4	5	6	7	8	9	10	11	12	13
Volume Fraction of rubber (Vr)	0.33	0.356	0.311	0.378	0.314	0.372	0.322	0.382	0.318	0.333	0.322	0.305	0.36

3.7. CONCLUSIONS

NR/Silica in general showed inferior technological properties except low heat build up, high flex resistance and reasonably good tear strength. ,NR/Silica/Silane system exhibited low heat build up, low compression set , high resilience and high tear strength which are of high technological relevace, whereas other properties were comparable to that of carbon black filled. NR/Silica modified with ENR though showed improvement in certain properties was found to be dependant on the percent epoxy content. NR/ENR/Silica/Silane of certain combination especially of low to medium epoxy content exhibited reasonably good technological properties. However further optimization is to be done.

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NR

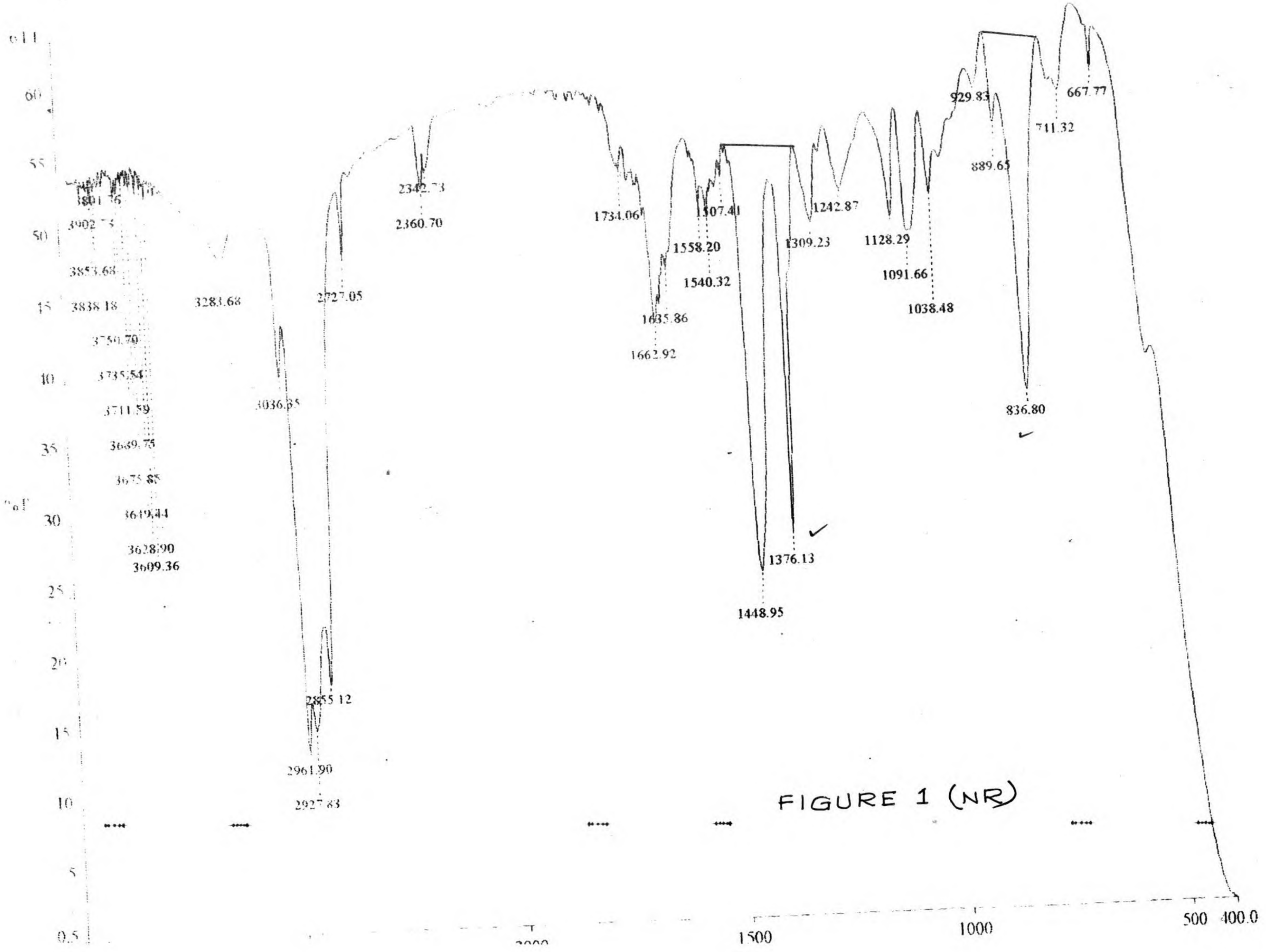


FIGURE 1 (NR)

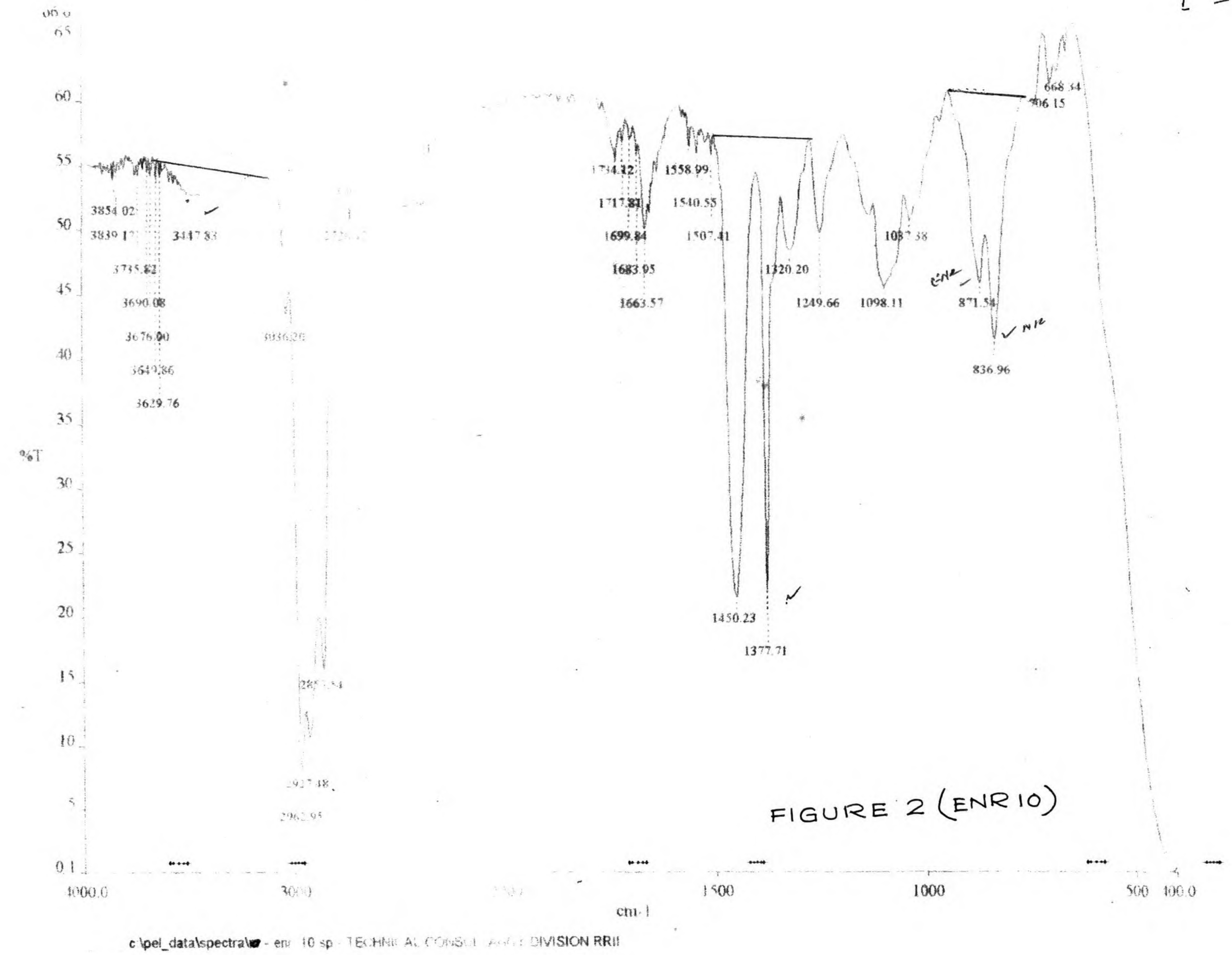


FIGURE 2 (ENR10)

17.5 17.5

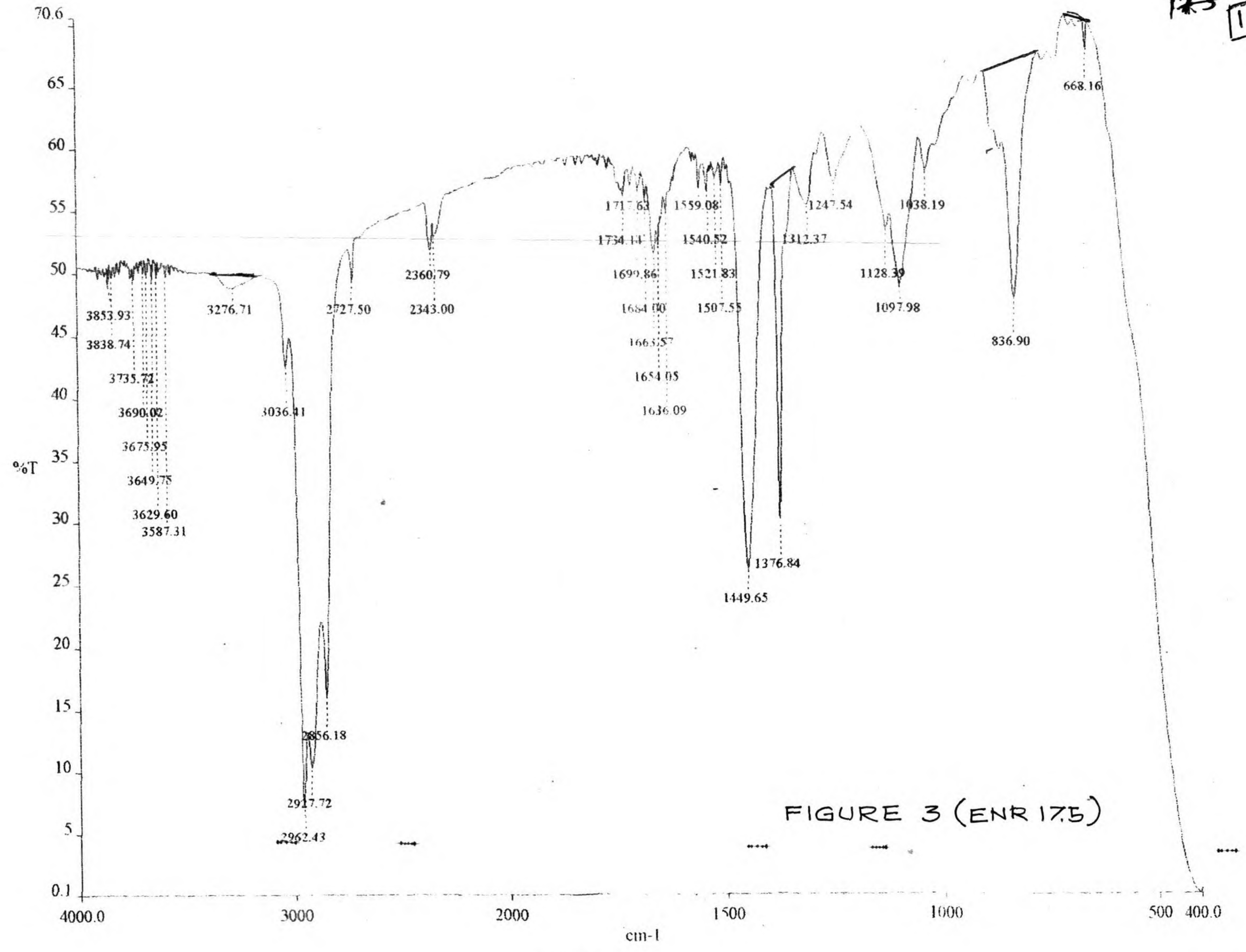


FIGURE 3 (ENR 17.5)

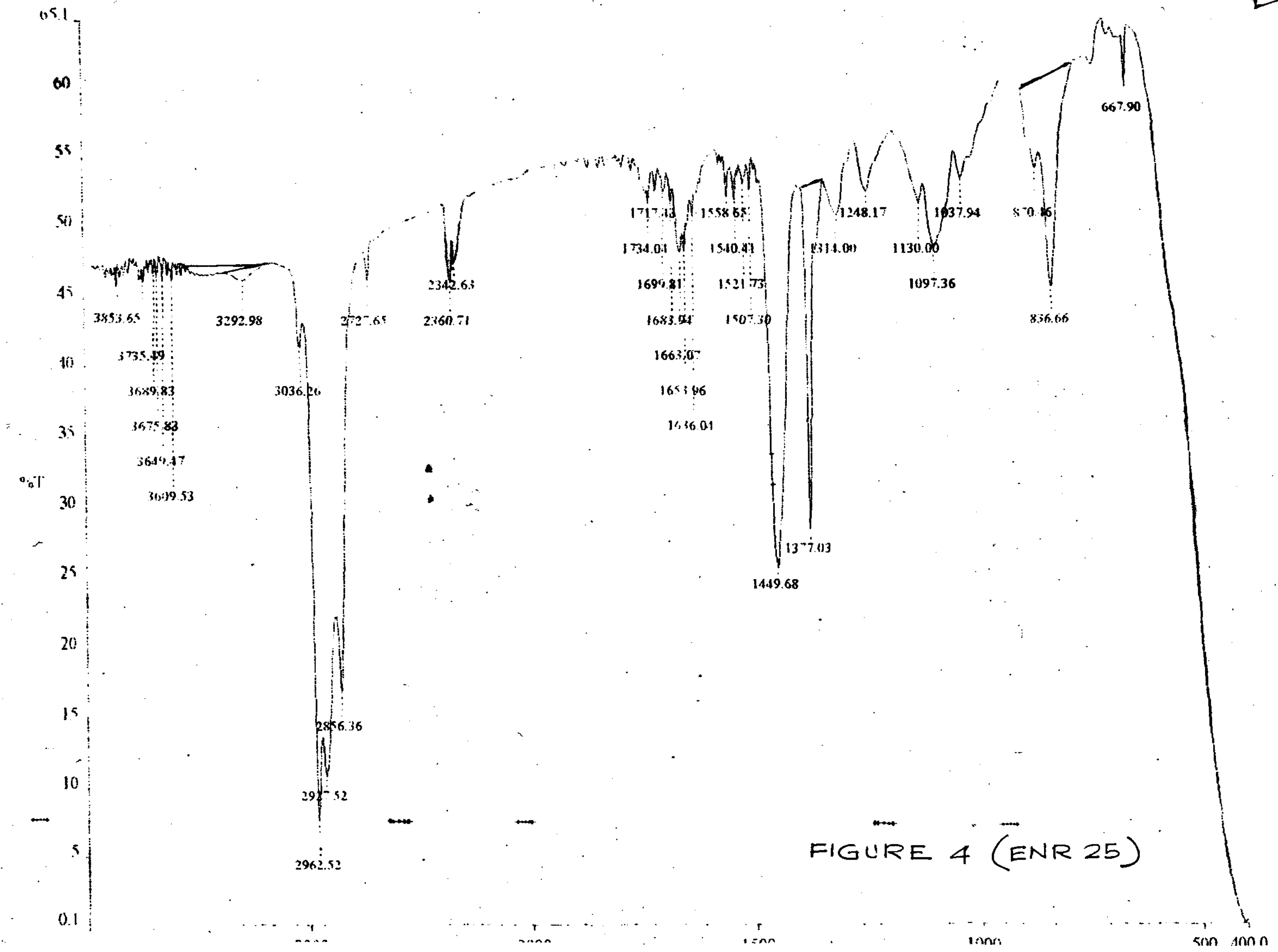


FIGURE 4 (ENR 25)

5

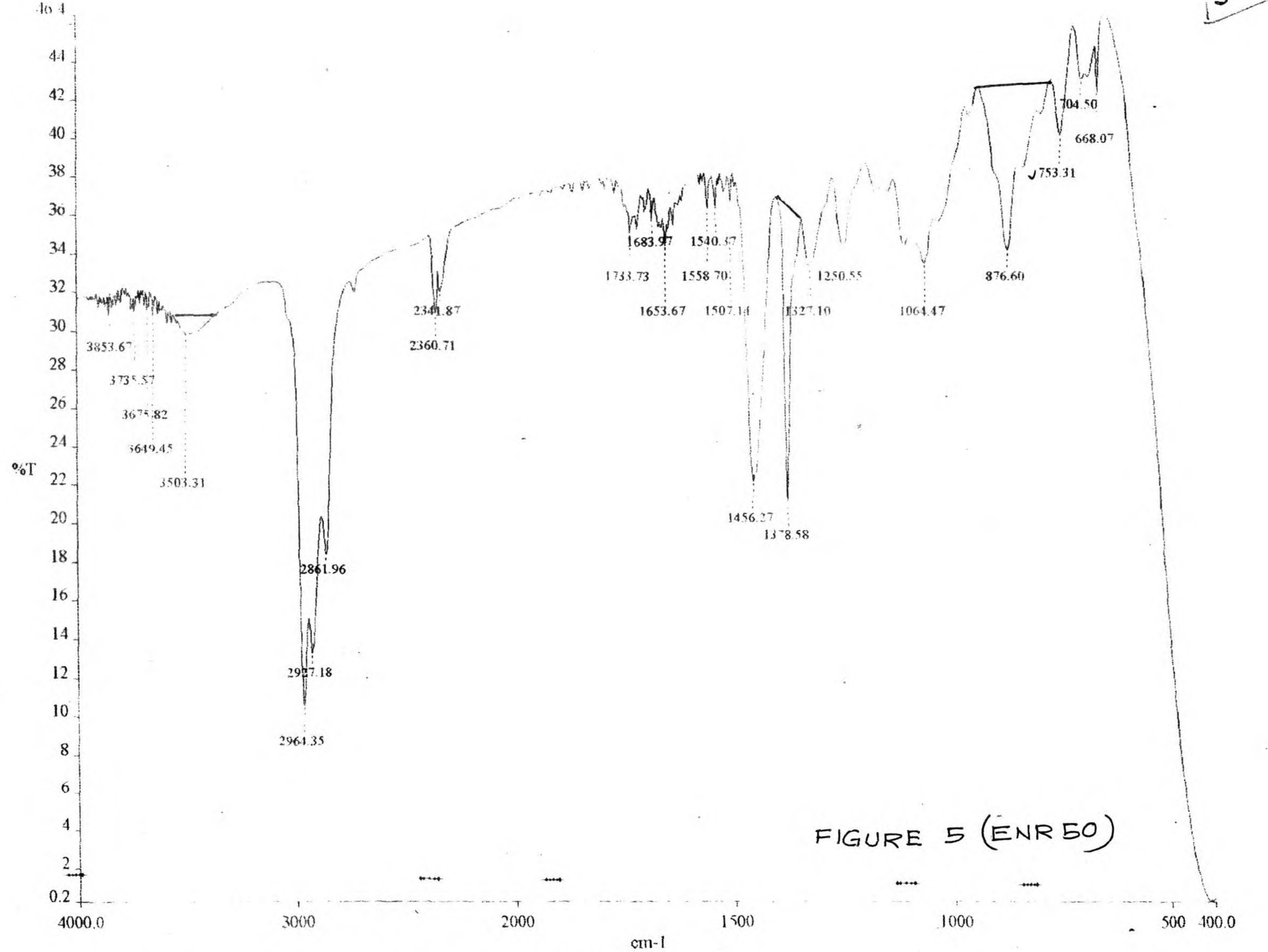


FIGURE 5 (ENR 50)

c:\pel data\spectra\enr 50.sp - TECHNICAL CONSULTANCY DIVISION RRII

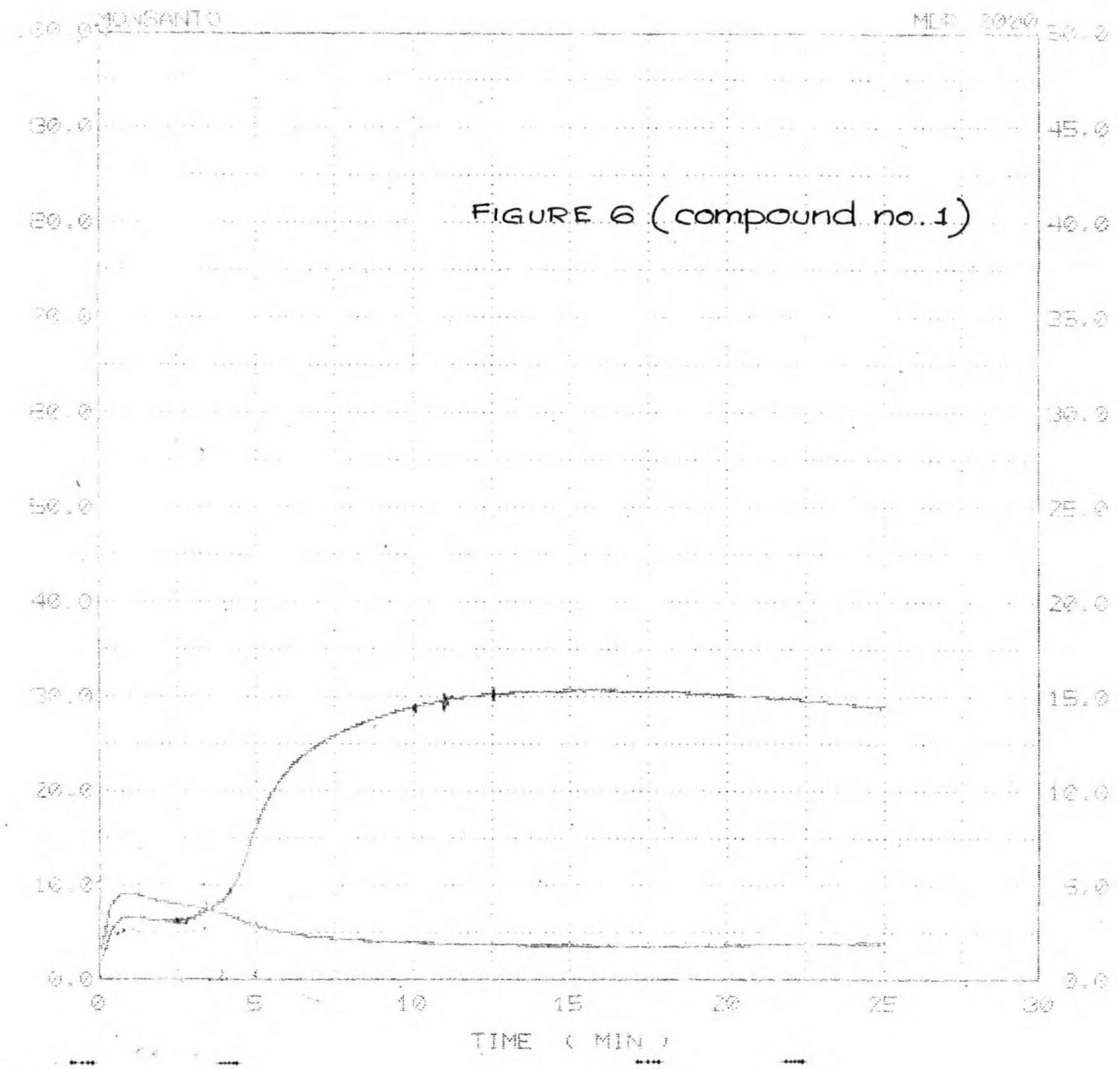


FIGURE 6 (compound no.1)

x Temp: 150.0 C ML: 2.13 dNm S' @ML: 1.75 dNm Tand @ML: 0.820
y Temp: 150.0 C MH: 30.79 dNm S' @MH: 1.85 dNm Tand @MH: 0.060
ts1: 0:14 m:s ts2: 0:19 m:s
t10: 0:24 m:s t50: 5:02 m:s t90: 8:58 m:s t95 → 10 minute

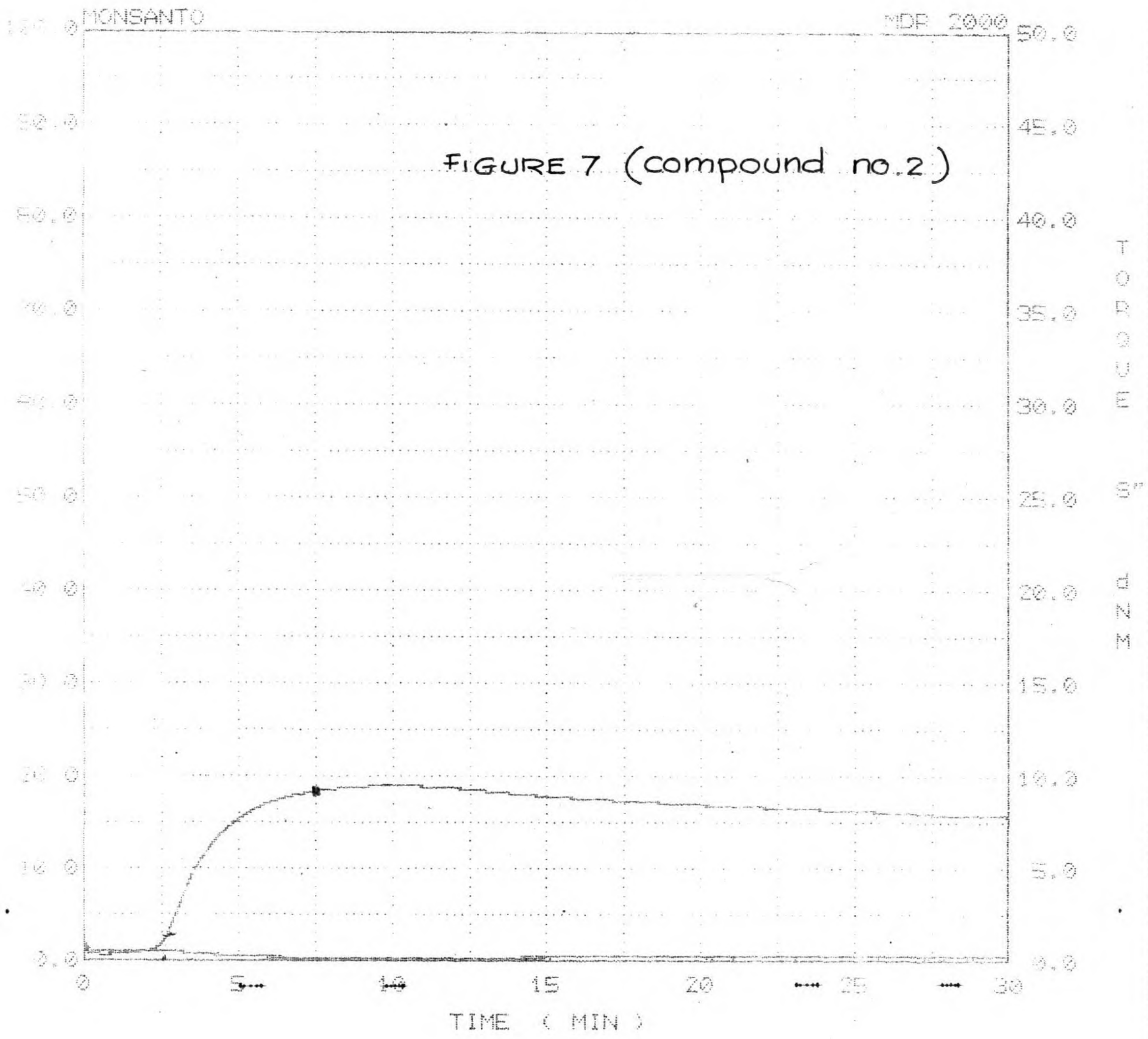


FIGURE 7 (compound no.2)

```
Temp: 150.0 C     ML:    0.74 dNm      S' @ML:   0.55 dNm     Tand @ML:  0.747
Temp: 150.0 C     MH:   19.08 dNm      S" @MH:   0.14 dNm     Tand @MH:  0.007
S1:     2:26 m:s  tS2:     2:41 m:s
10:     2:39 m:s  t50:     3:36 m:s    t90:    6:03 m:s
```

t95 = 7 min

=“4”

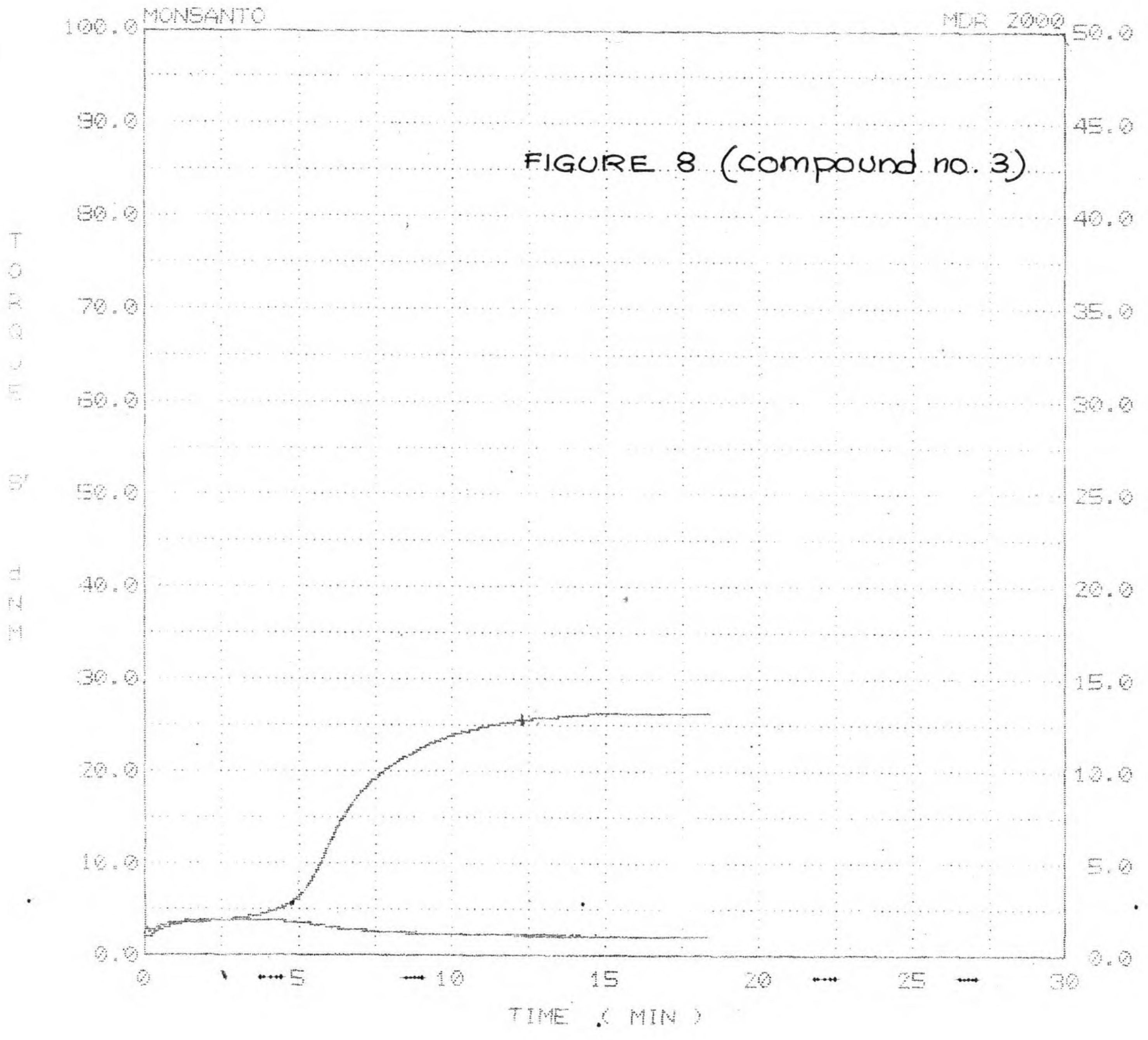


FIGURE 8 (compound no. 3)

(3) 13 12

Temp: 150.0 C ML: 2.05 dNm S' @ML: 1.37 dNm Tand @ML: 0.670
Temp: 150.0 C MH: 26.43 dNm S' @MH: 1.09 dNm Tand @MH: 0.041
ts1: 0:40 m:s ts2: 3:02 m:s
t10: 3:45 m:s t50: 6:19 m:s t90: 10:05 m:s t95 → 11 min

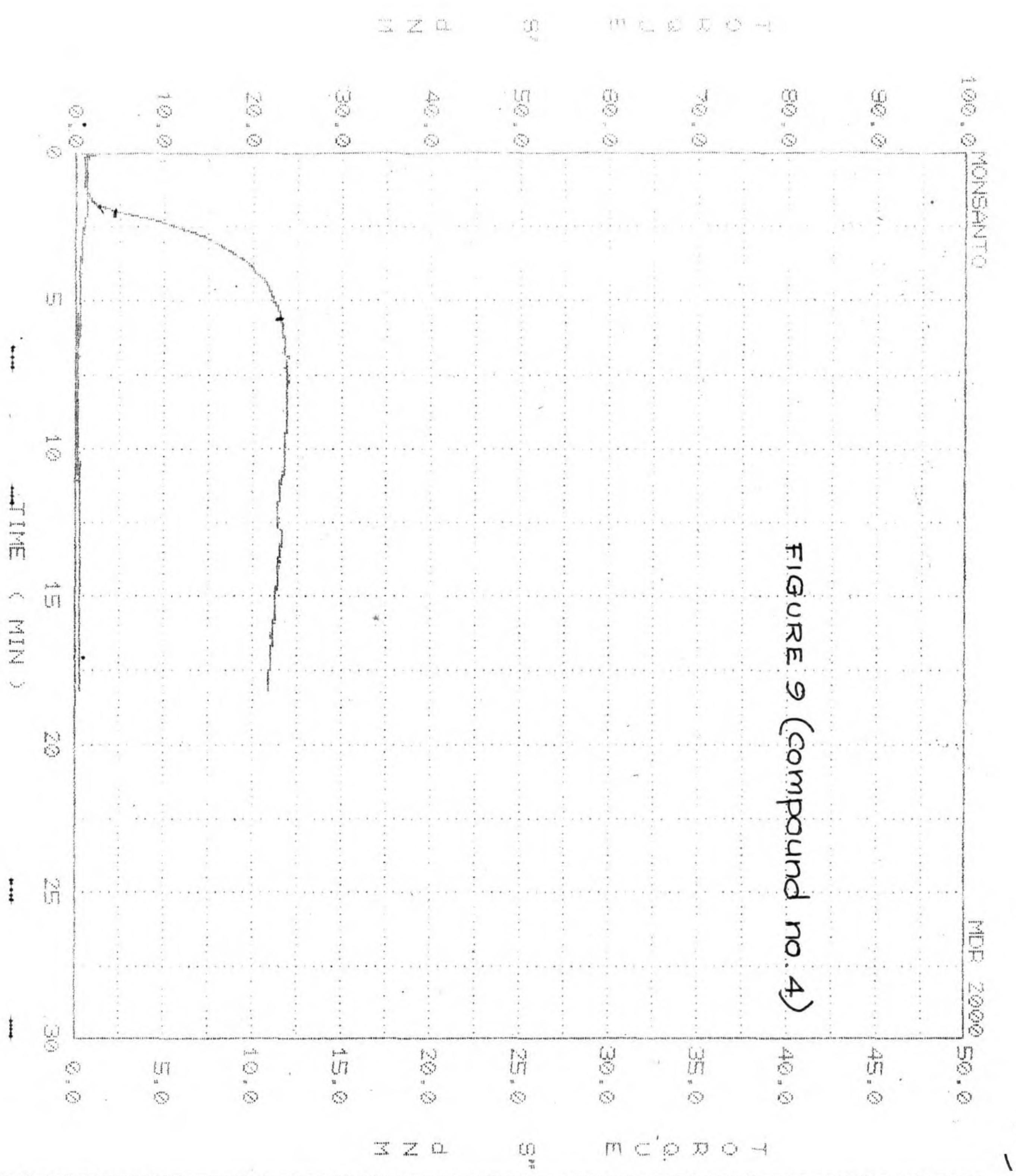


FIGURE 9 (compound no.4)

```
x Temp: 150.0 C     ML:    1.02 dNm    S" @ML:   0.64 dNm    Tand @ML:  0.625
y Temp: 150.0 C     MH:   24.09 dNm    S" @MH:   0.21 dNm    Tand @MH:  0.009
tS1:     1:39 m:s   tS2:     1:51 m:s
t10:     1:52 m:s   t50:     2:38 m:s  t90:     4:34 m:s
```

t95 → 5:30 (5½ min)

⑤

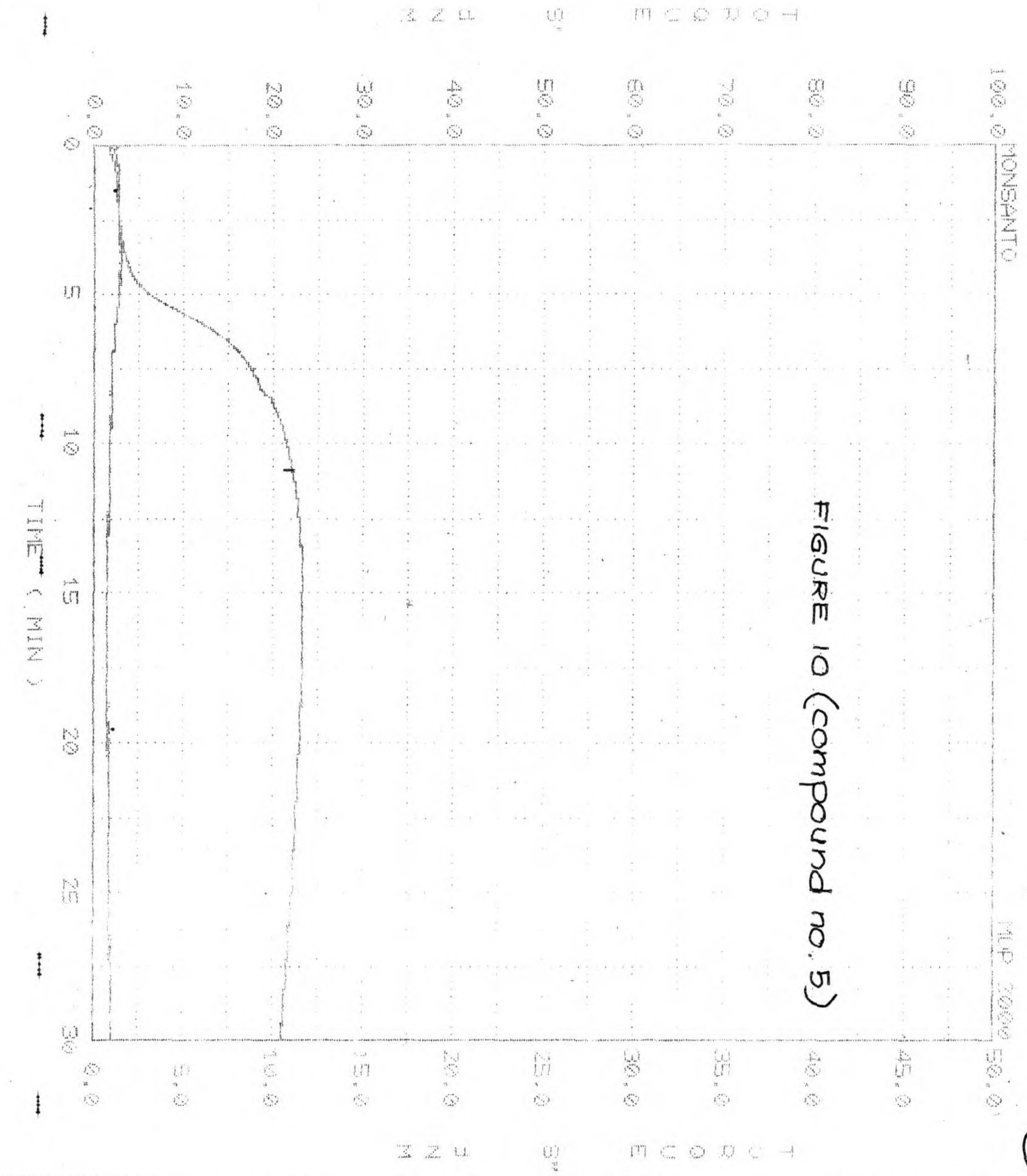


FIGURE 10 (compound no. 5)

7"1.

(4

x Temp:	150.0 C	ML:	1.80 dNm	S" @ML:	1.24 dNm	Tand @ML:	0.685
y Temp:	150.0 C	MH:	23.47 dNm	S" @MH:	0.81 dNm	Tand @MH:	0.035
tS1:	2:05 m:s	tS2:	3:56 m:s				
t10:	4:04 m:s	t50:	6:05 m:s	t90:	9:40 m:s		

t_{95} = 10:40s (10¾ min)

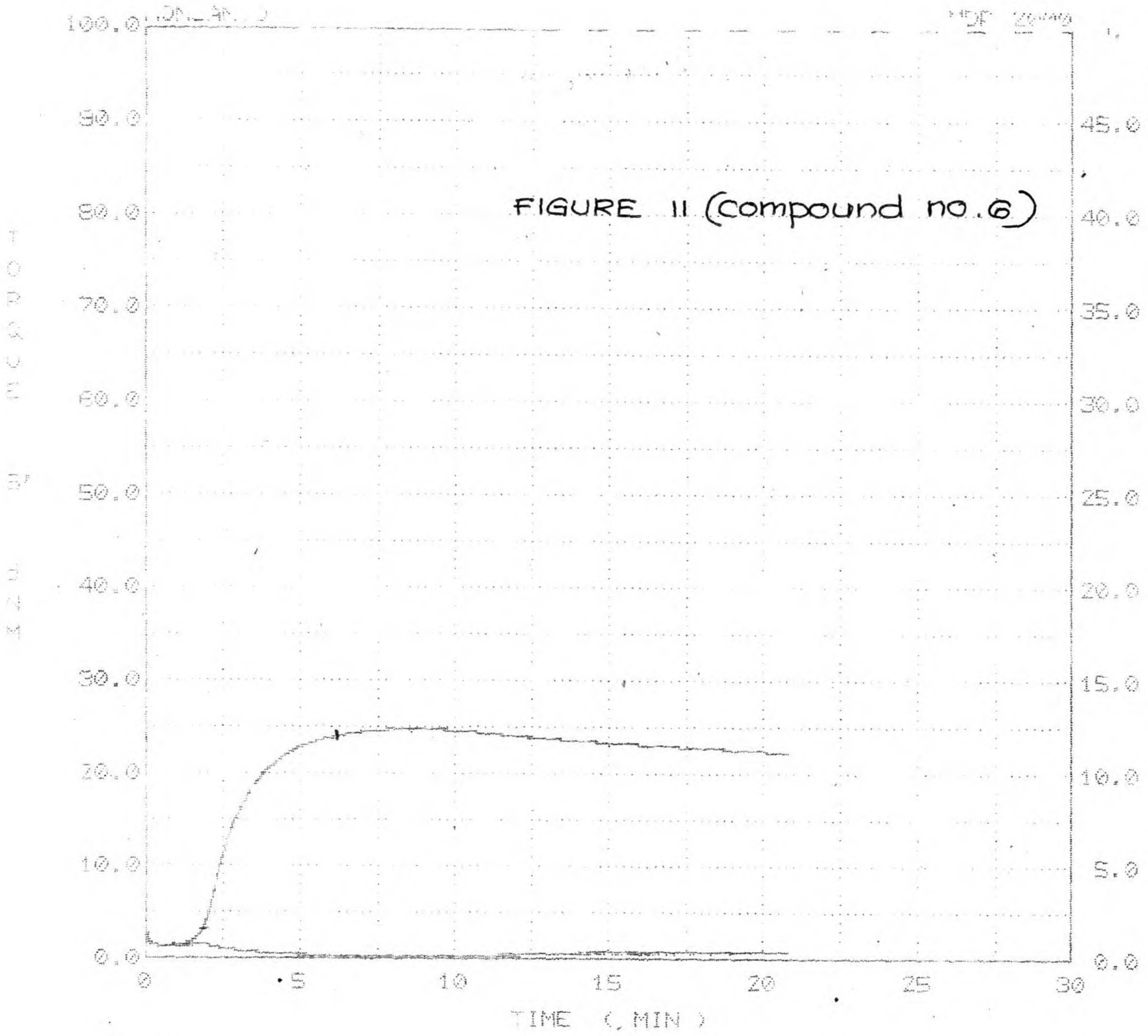


FIGURE 11 (compound no.6)

⑥

X Temp: 150.0 C   ML: 1.43 dNm   S" @ML: 0.72 dNm   Tand @ML: 0.50
Y Temp: 150.0 C   MH: 24.85 dNm   S" @MH: 0.16 dNm   Tand @MH: 0.
tS1: 1:44 min   tS2: 1:55 min
t10: 1:57 min   t50: 2:43 min   t90: 4:47 min   t95 = 5:43 (5 3/4 min)

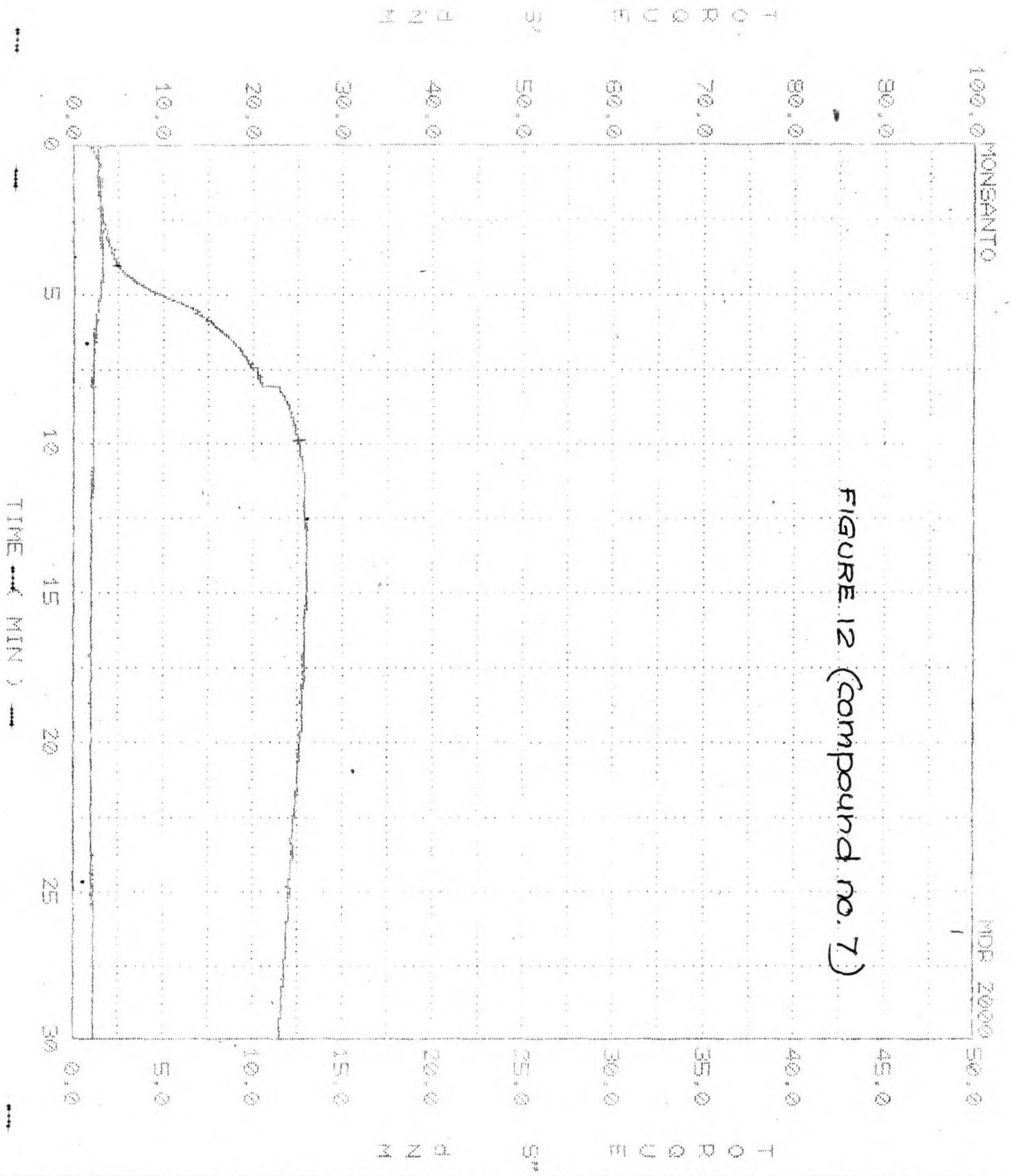


FIGURE 12 (compound no. 7)

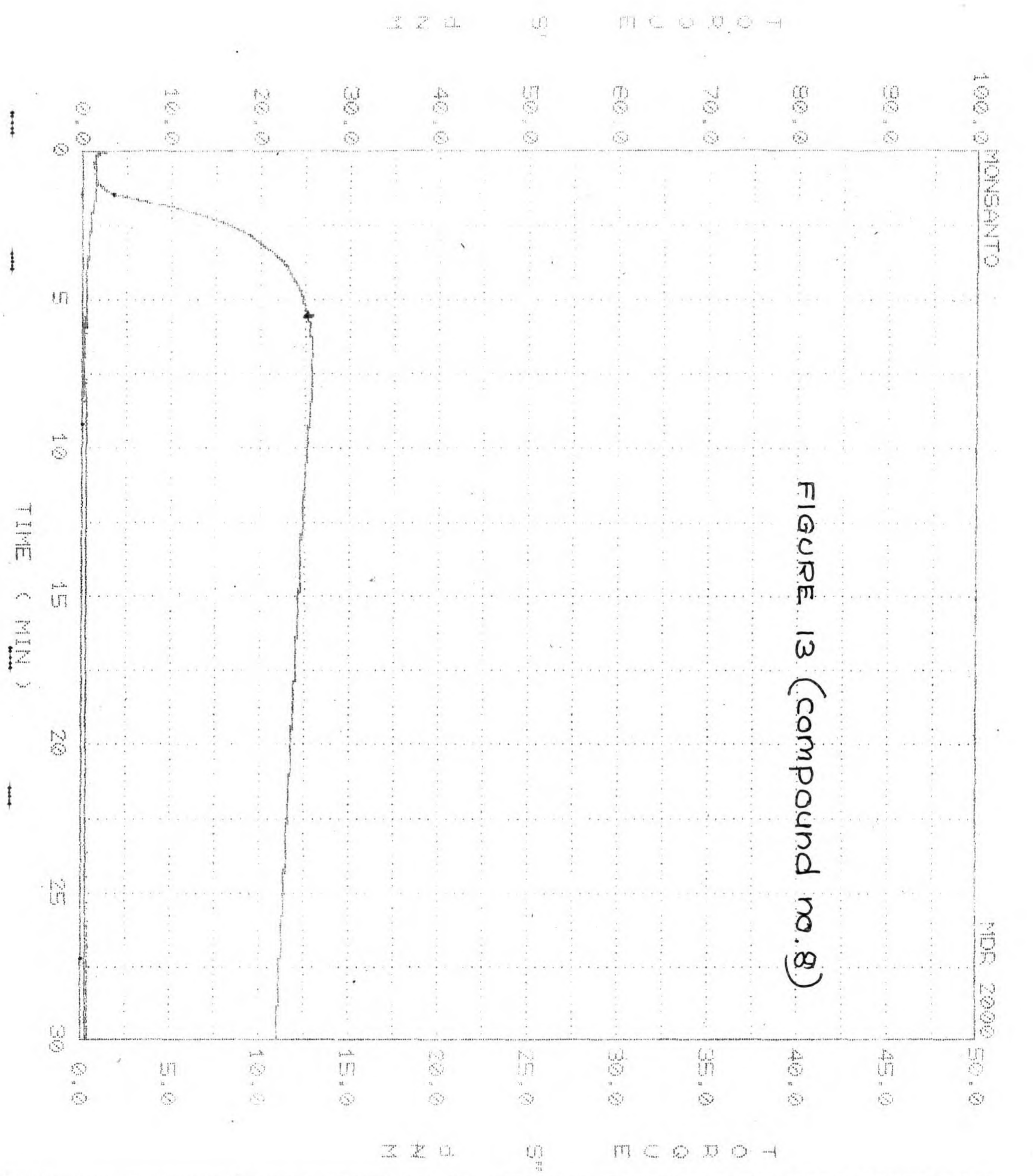
```
x Temp: 150.0 C      ML:     2.22 dNm      S" @ML:    1.45 dNm     Tand @ML:  0.655
y Temp: 150.0 C      MH:    26.10 dNm      S" @MH:    1.05 dNm     Tand @MH:  0.040
tS1:     1:22 m:s    tS2:     3:24 m:s
t10:     3:44 m:s    t50:     5:44 m:s     t90:     8:31 m:s
```

t_{95} → 9.30 (9½ min)

2

7

FIGURE 13 (compound no.8)



```
x Temp:  150.0 C     ML:     1.48 dNm     S" @ML:    0.77 dNm     Tand @ML:   0.523
y Temp:  150.0 C     MH:    25.95 dNm     S" @MH:    0.24 dNm     Tand @MH:   0.009
tS1:     1:18 m:s    tS2:     1:28 m:s
t10:     1:30 m:s    t50:     2:13 m:s    t90:       4:08 m:s
```

t95 = (5¼ min)

⑧

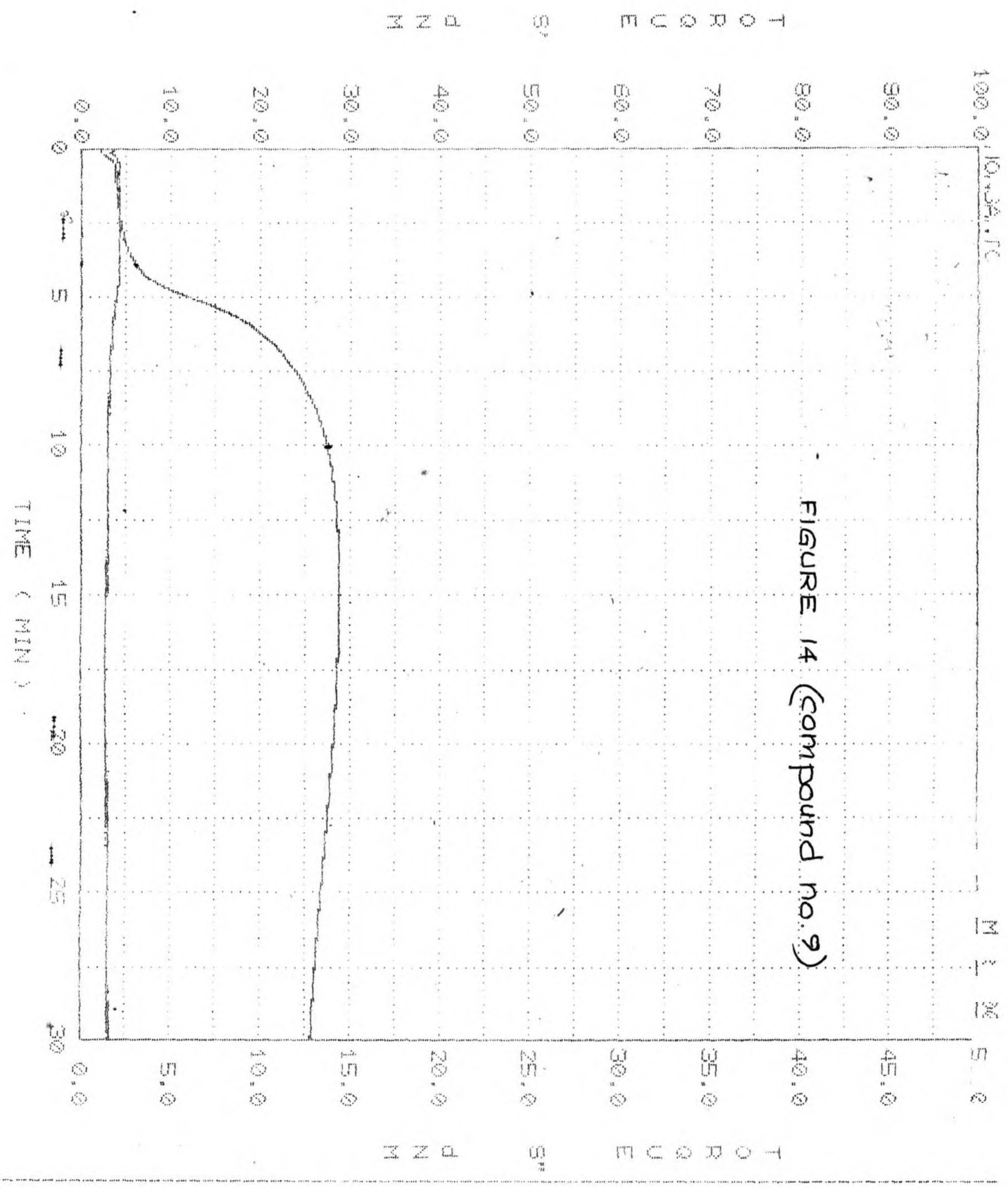


FIGURE 14 (compound no. 9)

```
x Temp: 150.0 C     ML:    2.28 dNm     S" @ML:   1.78 dNm     Tand @ML:  0.7o4
y Temp: 150.0 C     MH:   28.91 dNm     S" @MH:   1.50 dNm     Tand @MH:  0.0
tS1:    0:20 m:s    tS2:    2:03 m:s
t10:    3:01 m:s    t50:    5:26 m:s    t90:      8:48 m:s
```

~~[illegible]~~ t95 → 10 min

(2)

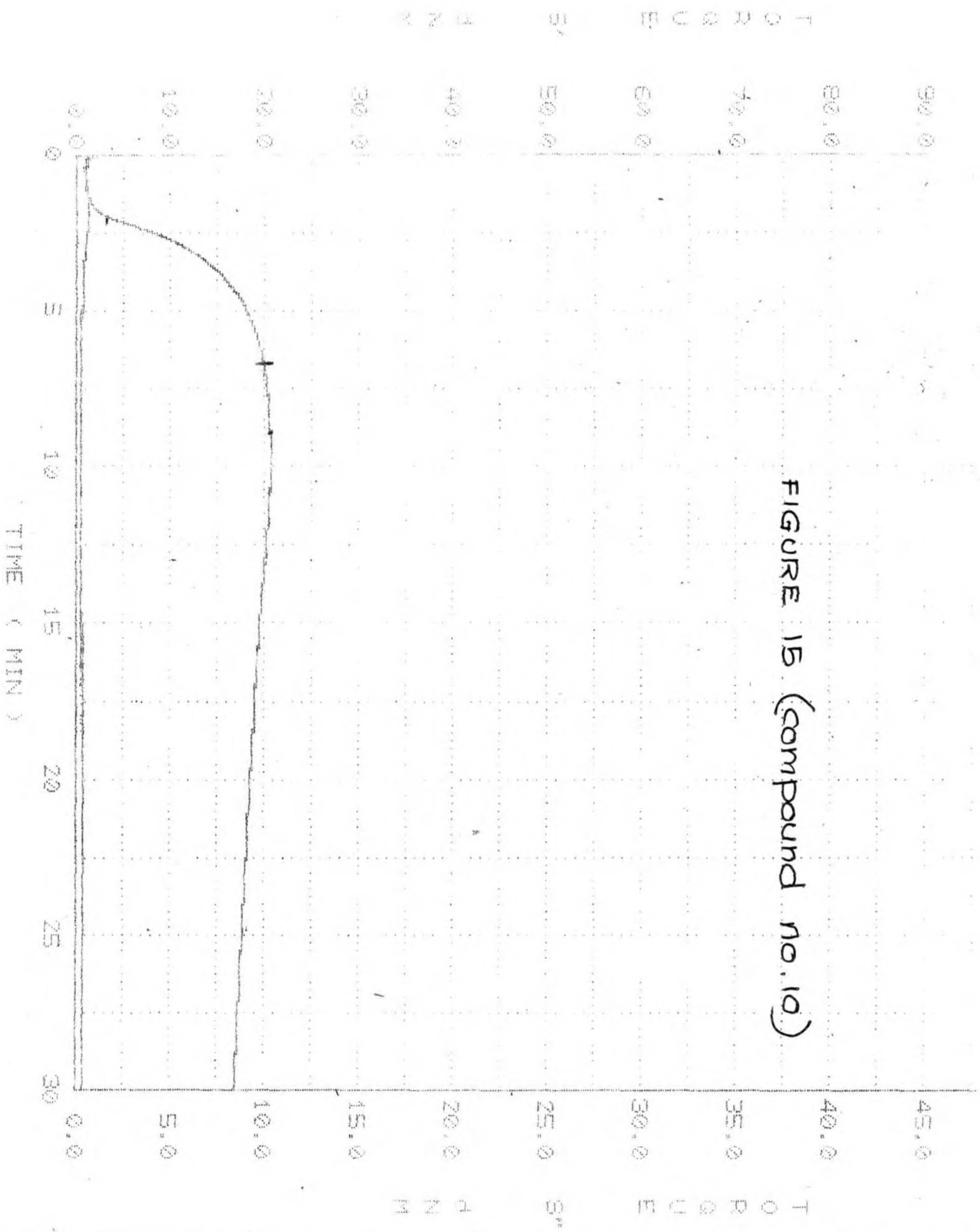
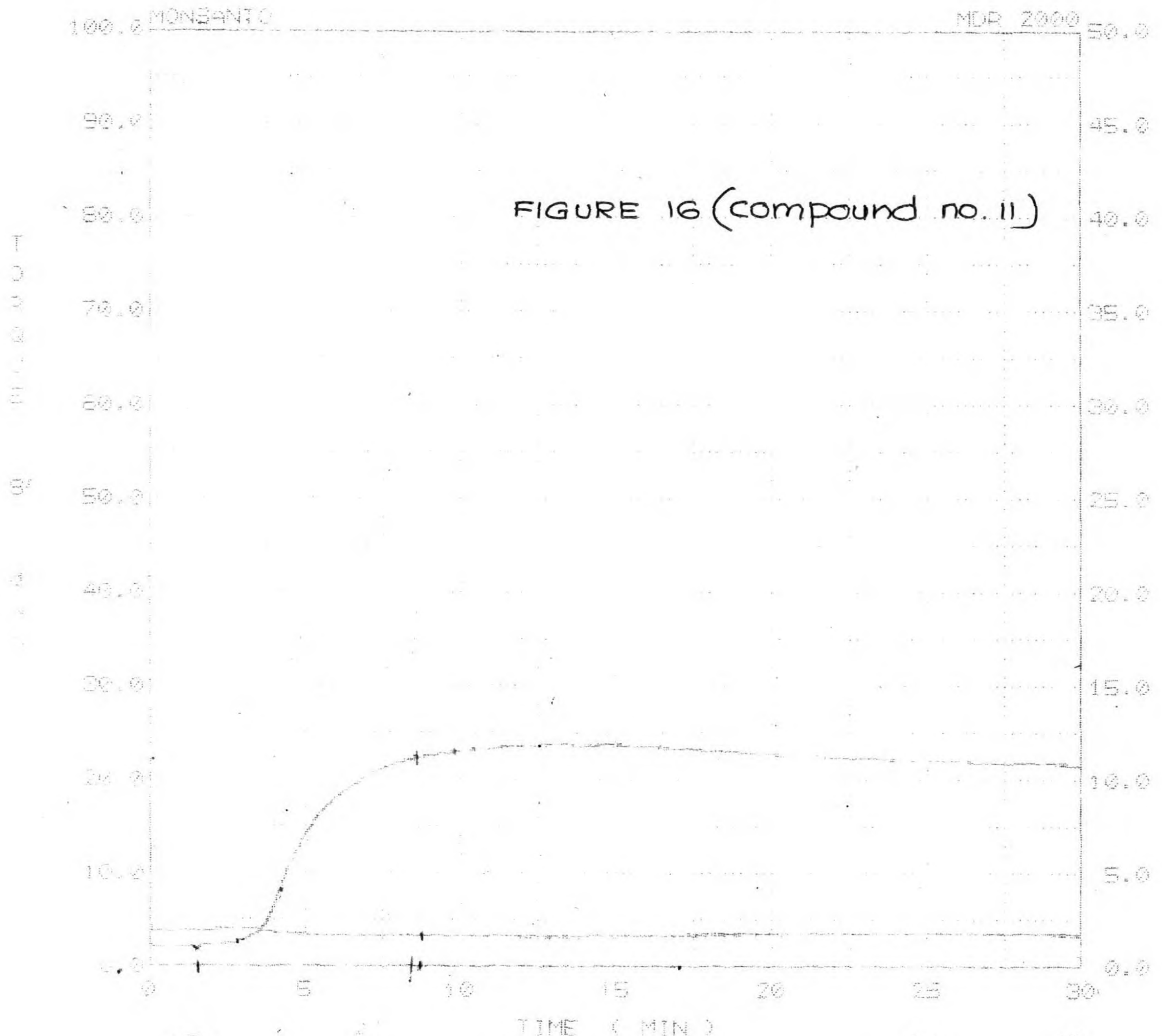


FIGURE 15 (compound no.10)

```
x Temp: 150.0 C      ML:    0.79 dNm      S" @ML:   0.62 dNm     Tand @ML:  °
y Temp: 150.0 C      MH:   20.82 dNm      S" @MH:   0.27 dNm     Tand @MH:
tS1:    1:42 m:s     tS2:    1:57 m:s
t10:    1:56 m:s     t50:    2:52 m:s     t90:     5:24 m:s
```

t95 → 6:30 (L'

FIGURE 16 (compound no. 11)



```
X Temp: 150.0 C     ML:   2.05 dNm     S' @ML:  1.92 dNm     Tand @ML:  0.958
Y Temp: 150.0 C     MH:  23.80 dNm     S' @MH:  1.54 dNm     Tanc @MH:  0.069
tS1:    3:11 m:s    tS2:  3:38 m:s
t10:    3:40 m:s    t50:  4:49 m:s     t90:     7:51 m:s
```

⑪

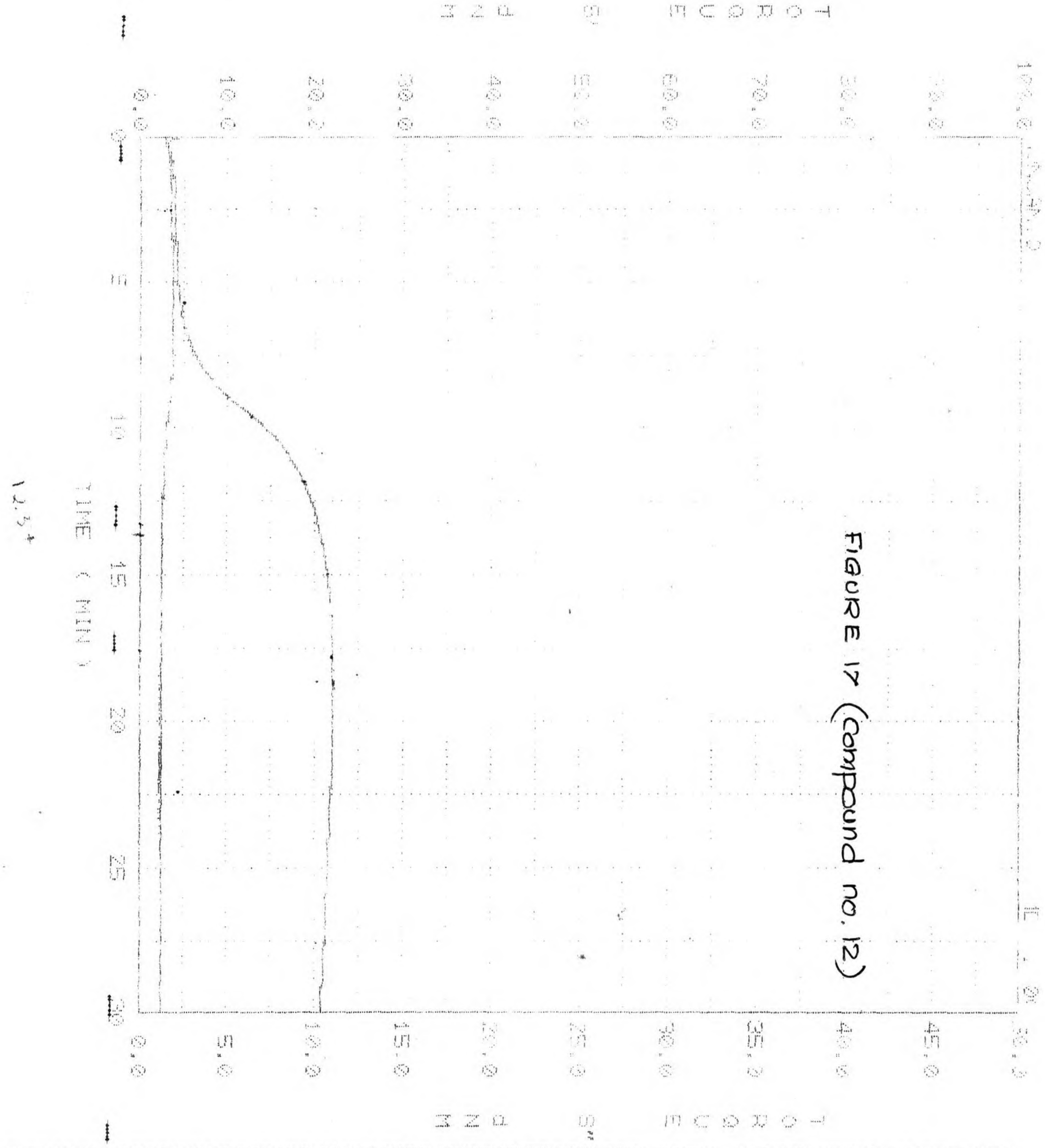


FIGURE 17 (compound no. 12)

```
Temp: 150.0 C     ML:     1.05 dNm     S" @ML:   1.70 dNm     Tand @ML:  0.5
Temp: 150.0 C     MH:    11.26 dNm     S" @MH:   1.26 dNm     Tand @MH:  0.0
1:    1:40 m:s    t30:    8:19 m:s
C:    6:11 m:s    t50:    9:24 m:s     t90:   13:00 m:s
```

(13)

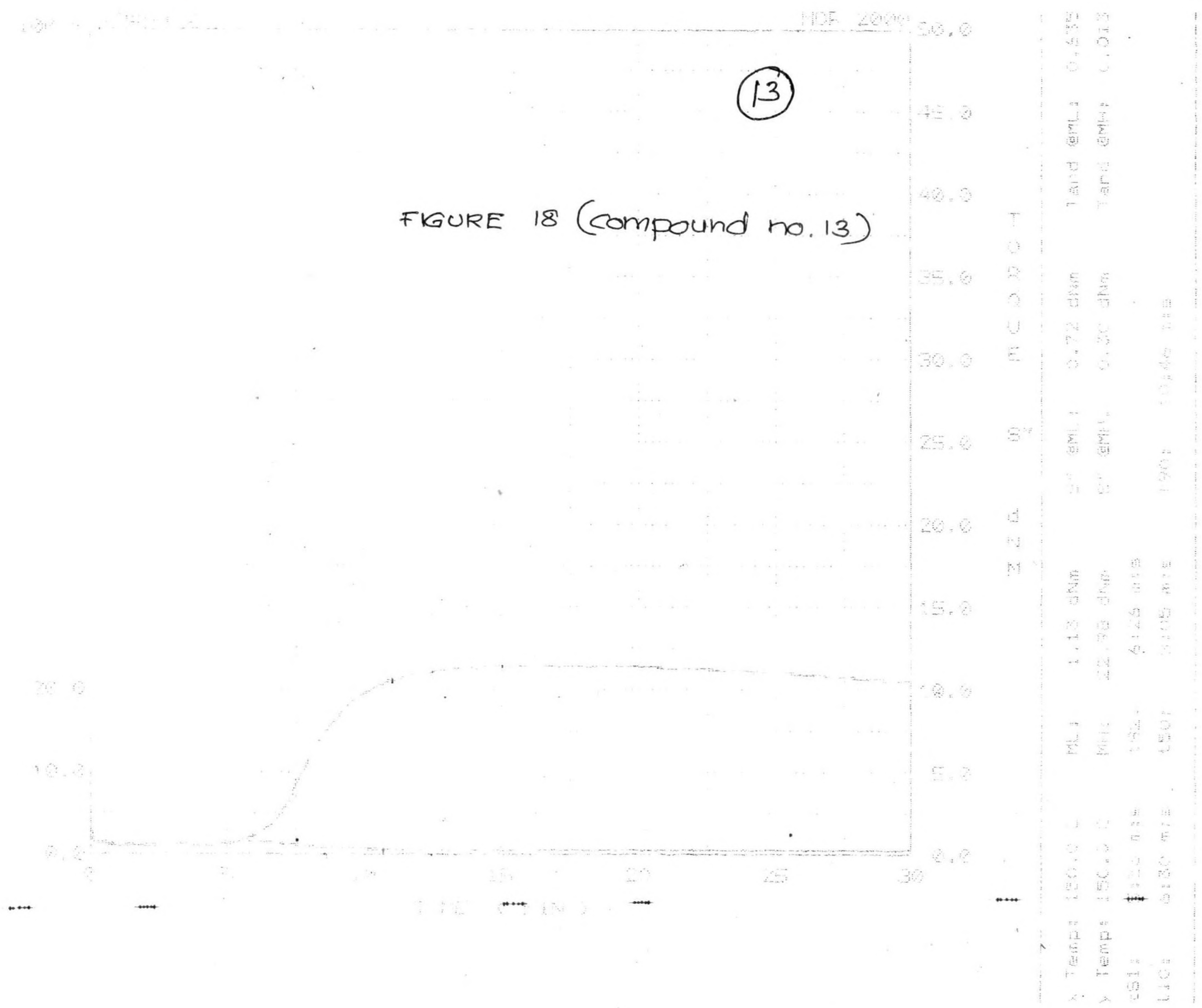


FIGURE 18 (compound no. 13)