STABILIZATION AND DEGRADATION OF SOME POLYMERS (PS, PMMA AND ABS)

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D E D I C A T E D T O 'H I M'

THE ANCIENT OF DAYS

WHO HEREUNTO HATH HELPED ME

" E B E N E Z E R " !!

A B S T R A C T

The degradation of stabilized and unstabilized polystyrene (PS) poly(methylmethacrylate) (PMMA) and Acrylonitrile - butadiene - styrene (ABS) have been investigated under conditions of oven ageing at 100°C, artificial UV irradiation and natural atmospheric weathering.

In the cases of PS and PMMA, the stabilizing effects of 3, 5-di-t-butyl-4-hydroxybenzylthioglycollate (DBHBT) and Zincdiethyldithiocarbamate (ZnDEC) have been compared with that of a commercial phenolic antioxidant Irganox 1076. Both the individual and two-component mixtures of these stabilizers have been studied using infra-red spectroscopy in monitoring the chemical changes taking place during degradation.

In all cases studied, the unstabilized films were found to degrade fastest. Under thermal degradation the efficiency of the stabilizers have been found to be in the order Irganox 1076 $\prec$ ZnDEC $\prec$ DBHBT. Results obtained showed ZnDEC and DBHBT as peroxide decomposers while Irganox 1076 act as a chain breaking antioxidant. Under UV irradiation, the stabilizing effectiveness of the stabilizers has been found to be in the order. ZnDEC $\succ$ DBHBT $\succ$ Irganox 1076.

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The two component mixtures of ZnDEC/DBHBT, Irganox 1076/ZnDEC and Irganox 1076/DBHBT have been found to show synergism.

Individual stabilizers of DBHBT and Tinuvin P have been incorporated into ABS films by physical mixing and the stability of the samples have been tested. Also, DBHBT has been grafted into ABS at the latex stage and the results obtained for films containing the grafted sthbilizers compared with those which have been physically mixed.

During the degradation of ABS, the polybutadiene content decreased while oxidative products containing hydroxyl and carbonyl groups were formed. The results obtained showed that DBHBT is a powerful thermal stabilizer but a rather poor UV stabilizer for ABS. On the other hand, Tinuvin P is a poor thermal stabilizer but a good UV stabilizer. The grafted stabilizer has been found to be much more efficient than the one which was physically mixed. The grafted stablizer was completely resistant to solvent extraction while the other one was extractable.

The mechanism of degradation of ABS has been proposed.

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1.0 INTRODUCTION

The stability of polymers is of critical importance and interest to manufacturers, and understandably, polymer degradation has received considerable attention.[1-4] Consequently, polymer technologists have directed their efforts towards improving the stability of the common polymers both during processing and subsequently during service life. In the course of such studies it has been found necessary to achieve a deeper understanding of the chemical mechanisms involved in the degradation of polymers and particularly, of the way in which chemicals interfere with the process. The latter is very essential in order to effect stabilization of the polymers by the use of chemicals called additives.

The basic mechanisms involved in oxidation of polymers and antioxidant action have been clearly recognized and decumented[5 - 6]. In order to understand modes of stabilization of polymers, the mechanism of degradation must first be understood.

1.1 Degradation of Polymers.

Degradation may be defined as the process of deterioration of materials resulting from the combined effects of the atmosphere, radiation, temperature, oxygen, ozone, water, micro - organism and other atmospheric agents. The manner in which each of the above factors cause deterioration of the plastics is determined by the chemical nature of the polymer and other basic constituents. The final effect on properties on the other hand

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is invariably the same, namely, development of colour and/or reduction of optical clearity, deterioration of mechanical properties, embrittlement and increased dieletric losses. With reference to the effect on the properties of polymers, the term degradation should therefore imply any number of reactions of polymer all leading to the loss of desired physical properties.

Some of the agents of degradation are as follow.

1.1.1 Hydrolytic Degradation

Some polymers exhibit a very noticeable sensitivity to moisture. Most detailed studies of hydrolytic deteriorations were carried out on polyesters and polyamides, although other macromolecules, such as cellulose and its derivatives have also received considerable attention[7].

1.1.2 Thermal degradation

Among polymer degradation reactions, those initiated by heat have been the most thoroughly and systematically studied [8]. Thermal degradation reactions are divided into two main classes referred to as random - and chain - degradation.

Random degradation can be compared to a reverse polycondensation in which rupture takes place at radom points along the chain while chain degradation is a depolymerization reaction involving successive release of monomer units from the chain ends.

1.1.3 Oxidation.

Industrial interest in the oxidation of polymers can be traced back at least to the middle of the 19th century. At that time, natural rubber and gutter percha came into common use mainly as water proofing and electrical insulating materials and it was realized that their deterioration in use was closely associated with the absorption of oxygen. Interest in oxidative degradation was not confined to the rubber and plastics industries, but even, the drying of paints and the rancidification of edible fats are oxidation processes.

Bolland and his co-workers[9] in 1949 and Bateman in 1954[10], have established that a radical chain reaction is involved in the oxidative degradation of polymers.

1.1.4 Ozone attack.

Ozone is one of the prime causes of deterioration of many polymers, particularly, elastomers. Thompson[11] was the first to observe that ozone generated in the laboratory caused cracking of stretched rubber.

Williams[12] also pointed out that the direct attack by ozone in the atmosphere on rubber items was responsible for the developments of cracks

1.1.5 Degradation by radiation

Atmospheric radiation comprises ultra-violet, visible and infrared light. Of these, UV radiation is the most harmful source of radiation to

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polymeric materials. The wavelength of light available on the the surface of the earth which has the most harmful effect on polymers is in the 290-400nm range of the UV spectrum. Most polymers contain chemical groupings or additives which can absorb radiation in this range and therefore, degradation reactions will take place. As in the case of thermal degradation, polymer molecules become activated or excited as a result of the UV light absorbed. This excess of absorbed energy causes breakdown of the weakest chemical bonds in the chain and active free radicals are formed which initiate the degradation process. The free radicals can produce unsaturation, chain-scission, or cross-linking of polymer molecules.

In the presence of oxygen, other chemical groupings such as carbonyl, carboxyl and peroxides may be formed.

1.1.6 Combined effects of temperature, oxygen and UV-light.

In the presence of oxygen oxidative degradation of polymers occurs whether the reactions are thermally or photolytically initiated. The effect of an increase in temperature is to accelerate further the rate of oxidation of polymers. Similarly, degradation by photo-oxidative reactions tend to increase with increased temperatures. The mechanism of degradation of polymers under the combined effects of heat and oxygen and of irradiation or photolysis and oxygen are referred to as thermal oxidation and photo-oxidation respectively.

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Having discussed the degradation of polymers, it is also appropriate to discuss various methods of preventing degradation.

1.2 Stabilization of Polymers.

The prevention of any or all of the degradative reactions mentioned above by the addition of chemicals (generally referred to as additives or stablizers) to the compounded polymer is known as stabilization. As the name rightly depicts, the attempt is to stabilize the polymer against the agents of degradation.

Some of the various types of additives employed in stabilizing polymers are discussed below.

1.2.1 Primary Stabilizers: Antioxidants.

These additives are presumed to retard or inhibit oxidation. The action of anti-oxidants is rather complex and diverse interpretations have been given in the literature. The general concensus of opinion is that antioxidants. (AH) interrupt the chain reaction by combining with the propagating free-radical species and thus forming non-reactive products. They act according to the mechanism.

$$\sim P^{\bullet} + AH \longrightarrow \sim PH + A^{\bullet} \text{ (inactive radical)}$$

where $P^{\bullet}$ is the propagating species and AH, the antioxidant.

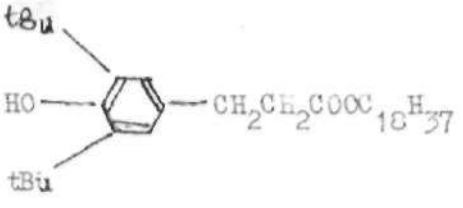
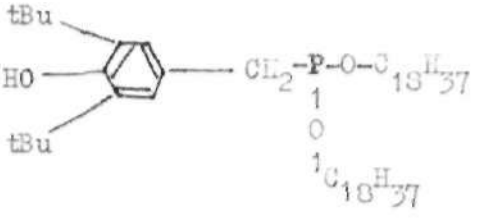
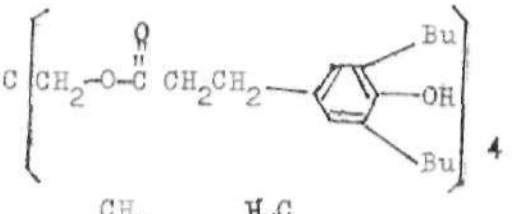
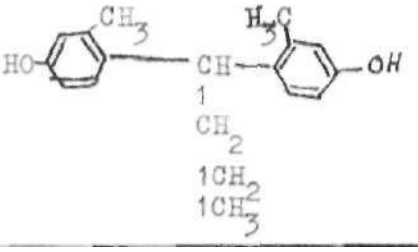
Most commercial primary stabilizers are either hindered phenols or aromatic amines. According to this mechanism the protection of polymer against thermal oxidation ceases when all the antioxidant has been consumed by the chain propagating species.

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The period over which this protection takes place is called the 'induction time' or 'induction period', and after this period, the degradation reactions proceed as if no antioxidant had been added.

The efficiency of an antioxidant can be expressed in terms of increased induction time over the unstabilized sample under conditions considered, or on the basis of its increased induction time over a wide range of temperatures. Examples of antioxidants available commercially are shown in table I.

1.2.2 SOME TYPICAL COMMERCIALLY AVAILABLE ANTIOXIDANTS

Chemical name	Structure	Trade name
Octadecyl-3,5-di-tertiary-butyl-4-hydroxyl phenyl propionate		Irganox 1076
Di (n-octadecyl)-3, 5- di-t-butyl-4-hydroxyl benzyl phosphate.		Irganox 1093
tetratrismethylene-3- (3', 5'- di - t - butyl-4'-hydroxyl phenyl) propionate methane		Irganox 1010
4, 4'-butylidene (6-t-butyl. cresol)		Santowhite powder

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1.2.3 Secondary Stabilizers: Peroxide decomposers

Another way of protecting polymers fro degradation is to remove peroxide radicals and to deactive hydroperoxides as, soon as they are formed. Many sulphur and phosphorus compounds can act in this way and the most common types are sulphides, thioethers, tertiary phosphites and phosphonates. Examples are zincdibutyl dithio carbamate and nickeldibutyldithiocarbamate.

1.2.4 Chelating Agents: Metal deactivators

Metals of variable valencies can enhance degradation of polymers by accelerating the rate of decomposition of hydroperoxides to active radicals. Hydroperoxides so formed are particularly susceptible to decomposition by metal ions such as

Cu^{+}, Fe^{2+} and V^{2+} (13, 14)

$$ROOH + M^{+n} \longrightarrow RO^{\bullet} + HO:^{\ominus} + M^{+(n+1)}$$

where M represents the metal.

Complexing these metal inns with bulky ligands creates sterric hinderance around the metal ion and prevents its interaction with active sites of the polymer chains. The presence of metal ion impurities in polymers can arise from many sources; e.g. catalyst residues of Ziegler-Natta or redox initiators, fillers, pigments etc.

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The most important class of chelating agents are compounds based on organic phosphines and phosphites and higher nitrogenated organic compounds e.g. melamine, bisasalicylidene diamines, oxamides, etc.

1.2.5 Synergistic Stabilizer Systems.

The term synergism is used to describe the combined effect of two or more stabilizers, which is greater than the sum of the effects of the individual stabilizers used in isolation. With antioxidant systems for instance a combination of primary and secondary stabilizers, are frequently used especially in polyolefins, and they provide a very efficient stabilization. Synergistic systems are even more widely used with poly (vinyl-chloride), PVC polymers. For instance Cd/Ba - and Cd/Ba/Zn stearates and laurates are notably good stabilizers and account for about 50% of all PVC stabilizers used commercially.[15,16]

1.2.6 UV Protecting Agents.

From the preceding discussion on the harmful effect of radiations on polymers, it can easily be deduced that to protect plastics against UV light by the means of additives, it would be necessary to reduce the energy level of the harmful radiations reaching the polymer. The additive must therefore be able to absorb UV light (without undergoing decomposition) more readily than the polymer, or the additive must interact and deactivate free radicals immediately they are formed.

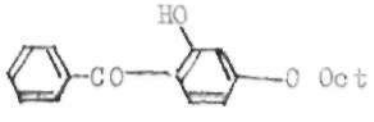
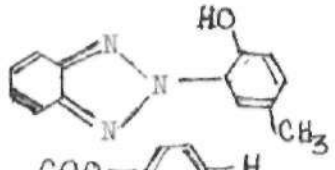
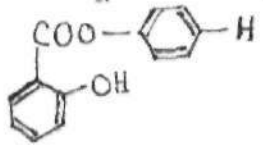
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Those additives capable of absorbing UV radiations are called' UV absorbers' or 'screaning agents' whereas those which can offer a stabilizing effect by interaction with radicals are called 'excited state quenclers'.

The use of UV radiation absorbers was introduced as early as 1945 by Meyer and Gearhart[17] to increase the service life of cellulose acetate. The first benzotriazole compound, Tinuvin P was introduced in 1956, while one year later the effectiveness of the first nickel-chelator as a UV stabilizer was discovered.

Examples of UV stabilizers available commercially are as shown in table II below.

1.2.7 TABLE II: COMMERCIAL ULTRAVIOLET STABILIZERS

Chemical name	Structure	Trade name
Hydroxybenzophenones e.g. 2-hydroxy-4-octyloxy benzophenone		HOBP
Benzotriazol-2-yl phenols e.g. 2-(2H-benzotriazol-2-yl)-p-cresol		Tinuvin P
Phenyl esters: e.g. Phenyl salicylate		Salol
Nickel compounds e.g Nickeldiethyldithiocarbamate.	 n = 2	NiDEC

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Most commercial UV stabilizers act assereaning agents, but quenching may also play a part in their function. The nickel chelates may act predominantly as quenchers, but they too, absorb a considerable portion of the incident UV light.

So far, only nickel compounds have found industrial application as quenchers[18]. Briggs and Hickeller[19] have found that the effectiveness of a series of experimental nickel complexes as UV stabilizers for polypropylene is similar to their quenching ability for anthracene, i.e. UV light is absorbed by the highly conjugated structure (of the complexes) and dissipated as harmless IR radiation by a resonance stabilization mechanism[20]

1.2.8 Condition for Effective Stabilization

To be an effective stabilizer, an additive must be able to dispose of its excitation energy without interacting with the polymer in harmful or destructive ways and without itself undergoing any photochemical reaction which would destroy its effectiveness. Energy is most harmlessly disposed off as heat; hence effective UV stabilizers must have structures that provide for a rapid cascade back to the ground state through thermally excited levels. For some compounds, this may involve a photoisomerization to some higher energy structure that reverts rapidly and efficiently back to the original structure with the loss of heat energy.

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The quantum efficiency for return to the unexcited ground state for the stabilizer must be greater than 0.99999; that is, less than one molecule of stabilizer can be destroyed for every 100,000 that are excited, otherwise, the stabilizer will itself be destroyed before it can extend the life of the polymer to a significant degree[41]. To achieve maximum effectiveness and minimum colour in a polymer, a UV absorber should have the highest possible absorbance from 290 to 400 nm but no absorbance above 400nm.

Although patent literature discloses a large number of classes of compounds which are claimed to meet the requirements for an effective ultra-violet radiation absorber, however, only four fundamentally different classes have achieved significance and are of commercial use. Some of these stabilizers are as shown in table II.

1.3 Selection of Additives: Technological Requirements.

The choice of any stabilizing additive for a particular polymer is governed largely by economic factors and by technical (or technological) considerations. Some of these factors influencing the industrial applications of plastic additives are:

1. High solubility of the stabilizer in the polymer
2. Low rate of stabilizer loss from the polymer through migration, exudation, volatilization, leaching, or other processes.

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1.4 Evaluation of Weatherability

To assess the weathering of plastics, both accelerated indoor methods and exposure to natural weather conditions are being used. The latter techniques are obviously to give more realistic results but are often irreproducible since the weather itself varies so much with the time of the year and location. Factors such as smoke, dust, fog, temperature, clouds, and the concentration of ozone in the upper atmosphere can all have a considerable effect on the amount of sunlight reaching the surface of the earth. The degradation of plastics under such ranging conditions is consequently very difficult to predict.

Accelerated indoor tests are more widely used for both mechanistic studies and formulation work, and artificial light sources which approximate very closely to the spectral energy of natural sunlight have been made commercially available in recent years. The xenon-arc light source, filtered through pyrex glass seems to reproduce very closely the sunlight spectrum in UV region, but other sources of UV radiations such as carbon-arcs, fluorescent lamps and mercury-arcs are also frequently used.

Exposures to these sources are often made intermittently in order to simulate day and night conditions and spraying with water droplets is sometimes carried out to reproduce the leaching effect of the additives by rain water.

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1.5 Monitoring of Ageing in Plastics

Irrespective of test methods used, the process of ageing is invariably monitored by chemical analysis and by changes in the physical and mechanical properties of the polymer. Techniques used include infra-red spectrophotometry to measure the increase in carbonyl and hydroxyl groups and the diminishing concentration of unsaturation, visible light spectrophotometry to determine the yellowness index (range 570-590nm) and the measurements of the destruction of any natural fluorescence or creation of new fluorescent species due to photo-decomposition reactions.

The deterioration of mechanical properties is normally assessed by monitoring changes that occur with time of exposure in properties such as tensile strength, impact strength, elongation at break and young's modulus.

Embrittlement test is another way of depicting extent of degradation. This test is carried out by flexing a piece of exposed sample through 180°, the sample being considered brittle if fracture occured.

1.6 Objectives and Scope of this Work

Although acrylonitrile - butadiene-styrene terpolymers, ABS, exhibit an extra-ordinary desirable combination of mechanical, thermal, chemical and electrical properties as well as ease of processing and a moderately low price, its outdoor performance as regards weatherability, is quite poor.

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Recently, some works have been reported on stabilization of ABS polymers against enviromental degradation [22-24], mostly thermal and photo-oxidation.

In the present work, Tinuvin P and 3,5-dit-t-butyl-4-hydroxybenzyl-thioglycollate. (DBHBT) have been incorporated into ABS by physical mixing as stabilizers and an attempt has been made in improving the thermal and photo-oxidative performance of ABS. An attempt has also been made in comparing the effectiveness of these additives as thermal and as photo stabilizers. The thermal and photo-oxidative performance of the stabilized polymers have been compared with that of unstabilized samples. Work has also been done on films (samples) which were processed and pressed and those which were processed and cast and the results ontained have been compared with each other.

Also, DBHBT has been incorporated into ABS by grafting at the latex stage. The photo-oxidative and thermal behaviour of this compound has been compared with the one that was physically mixed.

The effects of Irganox 1076, DBHBT and Zincdiethyldithiocarbamate (ZnDEC) and their combinations on the thermal and photo-stability of polystyrene and poly (methylmethacrylate) have been investigated.

The data obtained have been presented elsewhere in this thesis.

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C H A P T E R 2

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ACCOUNTS OF PREVIOUS WORKS	18 - 25

2.0 ACCOUNTS OF PREVIOUS WORKS

2.1 Polystyrene, PS.

Grassie and Weir[1] have reported that in the vacuum photolysis of polystyrene, (PS), the only gaseous product is hydrogen and that the polymer became insoluble and discoloured. Holland et el[2] discovered that crosslinking was concormitant with thermal oxidation and, as in photolysis this was accounted for in terms of combination of long - chain radicals. Yellow colouration was also observed to develop in PS under 2537A. radiation.[2,3] The colour intensity increased with time. It was suggested that the colour was due to conjugated unsaturation in the Polymer backbone.

Adams[4] demonstrated the formation of carbonyl groups in the oxidation of PS while Madorsky and strans[5] have reported that the products of the thermal degradation of PS contain small amounts of toluene, ethylbenzene and methylstyrene; while the principal products other than the monomer are dimer, trimer and tetramen. This evidence suggested unzipping from the chain ends.

Recently, Chaffar et al[6] showed that the photo-initiation of high impact polystyrene which has been initially subjected to heat treatment in the presence of air, as in normal processing operation, was due to the photolysis of hydroperoxides introduced into the polymer during the thermal treatment. They also found that phenolic antioxidants are weak retarders

Dithiocarbamates and phosphites were also found to be effective antioxidant both during thermal treatment and in photo-oxidation[7,8].

A general concensus on the mechanism of degradation is that both thermal-oxidative and photo-oxidative degradation of PS follow a free-radical mechanism[9-13]. Based on the rate and molecular weight measurements, the overall reaction could be explained in terms of initiation at the chain ends, followed by unzipping which produces monomer, intramolecular transfer from which dimer, trimer and tetramer are derived, and, intramolecular transfer which explains the rapid initial decrease in molecular weight. Crosslinking and insolubility may result from the combination of macro-radicals.

2.2 Poly(methyl methacrylate), PMMA

The degradation of PMMA was extensively investigated by Grassie and Melville[3,14]. They showed that quantitative yields of monomer are recoverable on heating. The principal degradation processes were revealed by a combination of molecular and rate measurements. Cowley et al[15] also showed that quantitative depolymerization of PMMA to monomer can be initiated by 2537A. radiation. They found the change in molecular weight and the rate characteristics to be identical to those of thermally initiated reaction.

Wall, Madorsky and co-workers[9,10], have examined the products and overall characteristics of the depolymerization of a variety of polymers

including PMMA and have been able to make interesting correlations between polymer structure and the nature of the depolymerisation reaction. They discovered that there was no other volatile product except the pure monomer. It has also been demonstrated that UV irradiation of PMMA films resulted in a rapid decrease in the viscosity average molecular weight of the polymer.[16]

Available evidences support a free-radical mechanism of degradation. Allison[17] demonstrated that the photolysis of PMMA results in scission of the polymer by a radical process. Golike et al[18] and, Davies and his co-workers[19] also found that the degradation of PMMA followed a free-radical depolymerization mechanism. Grassie and Melville [3,14] were also able to demonstrate directly the radical nature of the reaction by the powerful inhibiting effect of traces of 1,4-diaminoanthraquinone. In addition, the single monomeric product and continuously decreasing rate were used as evidences that transfer reactions are absent and that the overall process can be regarded simply as a reverse polymerization reaction.

On stabilization, Burlant[20] demonstrated that incorporation of styrene as a comonomer in the polymer chain decreased PMMA degradation, presumably by an energy transfer process. Lead stearate and aromatic compounds were also found to act as protectants for PMMA by a similar energy transfer process[21]. Some stabilization has been achieved by copolymerization with small concentrations of a second monomer which is incapable of being

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liberated from the polymer chain by depolymerization. Acrylates are found to be particularly effective and have been used industrially for this purpose, As little as 1 part in 400 parts PMMA of copolymerized acrylonitrile was found to inhibit degradation completely. Grassie and Melville[3], while attempting to elucidate the mechanism of degradation found that 1,4-diaminoanthraquinone powerfully inhibited the degradation of PMMA.

The addition of compounds such as allythiourea, aniline, benzoquinone and 8-hydroxyquinoline was found to decrease the chain cleavage of PMMA by radiation[23]. This protective action was believed to be accomplished principally by direct action through energy transfer rather than by competition for free radicals.

2.3 Acrylonitrile-butadiene-styrene terpolymers, ABS.

Documented reports on ABS are quite few and recent.

Shimada and Kabuki[23] found that in the early stages of thermal oxidation of ABS films, the polybutadiene (PB) content decreased and oxidative products containing hydroxyl and carbonyl groups were produced. In their view, the initiation process was thought to involve mainly, the production of hydroperoxides induced by radicals and that subsequent processes were initiated by the decomposition of the hydroperoxides. Scott[24] showed that the rubber component is very susceptible to oxidation and that photolysis leads to cross-linking of the rubber phase, accompanied by

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scission of the graft between the rubber and the polymer matrix. This was also followed by loss of impact strength. Reports of other works indicated that thermal processing activates polybutadiene based polymers to photo-oxidation by introducing photo-sensitizing hydroperoxides into the polymer. Carbonyl groups formed during thermal processing thus act as photo-initiators for photo-oxidation[6,25].

Davis and Gordon observed that exposure of ABS films to oven ageing, artificial UV radiation and to natural atmosphere led to a marked decrease in the concentration of polybutadiene unsaturation accompanied by the build up of hydroxyl and carbonyl groups.

For stabilizing ABS, a phenolic anti-oxidant, Irganox 1076, and NiDBC have been found to offer some protection during processing and in service[24]. The combination of the two was found to be synergistic for thermal oxidation. It was also discovered that a concentrated masterbatch of up to 8% W/W ABS, of a combination of phenolic antioxidant BLBM (3,5-di-t-butyl-4-hydroxybenzyl mercapton mercaptan) and a thiol UV stabilizer ABHPT (4-benzoyl-3-hydroxyphenyl-O-ethyl thioglycollate) gave a synergistic mixture which has a UV lifetime five times that of commercially stabilized ABS and over seven times that of the unstabilized product.[24]

Kolawole[27] showed that the combination of BHBM and ABHPT, added as bound masterbatches are effective synergists for ABS and that 2-hydroxy-4-

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octyl-oxybenzophenone also imparts considerable protection to ABS during UV irradiation Fahan,[20] not only demonstrated that 2,4-dihydroxybenzophenone acted as a UV stabilizer for ABS, but also that grafting increases the efficiency of UV absorbers by reducing volatility and increasing compatibility and permanence. Similarly, Scott[24] also showed that antioxidants can be bound unto rubber to give solvent and detergent resistant vulcanisates without sacrificing antioxidant efficiency.

The general agreement seems to indicate that the oxidative degradation of ABS proceeds through the destruction of the unsaturation in the polybutadiene content, and that protection is most effective when the stabilisers are grafted to the rubber backbone of the ABS polymers.

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3.1 Materials

Chloroform (Analar grade), used as solvent for polystyrene, PS, and poly (methylmethacrylate), PMMA, was supplied by BDH. Irganox 1076, a phenolic antioxidant was supplied by Ciba - Geigy and used without further purification. The zincdiethyldithiocarbamate (ZnDEC) was prepared by double decomposition of a 10% solutionof the corresponding sodium salt with a saturated solution of the transition metal sulphate.

3,5-di-t-butyl-4-hydroxybenzylthioglycollate DBHBT was kindly supplied by Dr. A. G. Kolawole.

The polstyrene and poly(methylmethacrylate) were supplied by RAPRA while the acrylonitrilebutadiene-styrene terpolymer used was supplied by Borg-Warner Chemicals Limited as Cycolac R211.

3.2 Processing of ABS polymers.

Unstabilized ABS was mixed in the RaPRA torque rheometer model MK3 for three minutes at 190°C at high speed and a ram pressure of 40psi. Similarly, ABS with Tinuvin P and ABS with DBHBT were processed as above. Samples containing the additives were processed for different periods of time between 2 and 10 minutes.

3.3 Film pressing of the processed samples

The pressing of the ABS films was carried out in two stages

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3.3.1 Pre - pressing.

About 2g of processed samples were pressed (using cold press) between two glazing plates using a pressure of 40 psi. At this stage thick films were obtained.

3.3.2 Compression moulding

Four specimens of 0.5g each were out of the thick, pressed film and placed between the glazing plates between which were formerly placed two cellophane papers. The specimens were preheated in the press at 190°C for 1½ minutes without pressure. They were then pressed at 60 psi for another 1½ minutes. At this stage, thin films of thickness of 5×10^{-3} cm were obtained.

3.4 Casting of films.

Solutions of polystyrene and poly (methylmethacrylate) in chloroform and ABS in dichloromethane were prepared. Films were prepared from 2% solutions of the polymers by pouring a measured volume on a mercury surface in a desicator glass basin and allowing to evaporate at room temperature. For each casting, clean mercury was always used.

In order to obtain even films from ABS solutions, it was necessary to filter the small amount of gel which was normally present before casting

For polystyrene and poly (methylmethacrylate) the stabilizers were added by weighing the required amount of the additive to the base polymer,

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which were then thoroughly mixed together before dissolving in chloroform.

3.5 Method of Analysing Degradation

It is obviously preferable, where possible, to make the comparison of the weatherability of commercially available plastics with reference to those properties of practical importance especially the mechanical properties. However, the marked dependence of mechanical properties on test procedure and testpiece-history, unrelated to weathering introduces scatter into test results to such an extent that assessment of comparative stability is very difficult, if not impossible.

Because of the non-reproducebility and dependance of results obtained from mechanical studies on test method and testpiece-history, the anthor has directed his attention to the monitoring of the chemical changes occuring during degradation and ways of combatting the same i.e, stabilization by the use of infrared spectroscopy.

3.6 Infra-red Analysis.

Examining thin films by transmission spectroscopy permits the course of degradation reactions to be followed without damage to, or interference with, the test area. Furthermore, being a non-destructive test it permits the same area to be used repeatedly for tests, this eliminating from the results, the specimen-to-specimen variation inseperable from destrustive test data. This method is more reliable than the mechanical

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property measurements and is also preferable to methods suggested of avoiding the difficulties with the mechanical property measurements. One suggested way of avoiding these difficulties has been to machine off the degraded surface and analyse it[1]. Another is to examine the surface in-situ by the infrared method of attenuated total reflection, ATR[2], but this method is only semiquantitative.

3.7 Preparation of test samples

Samples for infrared test were prepared as follows.

Cardboard was measured and cut out so as to fit exactly into the sample holder of IR machine. Then, a rectangular hole was made at the centre of the cardboard so as to be exactly in the path of the IR beam. Films were then cut out to overlap the rectangular hole made in the cardboard and then stapled,. The films were cut out in such a way that they are larger than the rectangular holes of the cardboard, so that the overlapping portions could be used for embrittlement tests. The sample tests were then subjected to weathering conditions and the degradation followed by running I.R. spectra at intervals.

3.8 Outdoor Exposure: Natural weathering.

For outdoor exposure, the test samples were mounted on Retort stands outside the chemistry department of Ahmadu Bello University, Zaria, Nigeria. Chemical changes occuring during exposure were monitored by infrared

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measurements and the time to embrittlement was recorded.

3.9 Oven Ageing.

Accelerated thermal oxidative degradation of the films were carried out by mounting the samples on the specially prepared cardboard holders which were suspended with copper wires in an air oven thermostatted at 100°C.

3.10 UV Studies.

Accelerated indoor weathering of the polymers were carried out with a UV fluorescent lamp of wavelength 254nm in the Radiochemistry Laboratory.

3.11 Infra-red Spectroscopy Measurement.

Measurement of carbonyl, hydroxyl and trans -1, 4- polybutadiene absorbance:

For these measurements, Perkin Elmer Model 1000 infra-red spectrophotometer was used. Specimens of 5×10^{-3}cm thickness were used and the spectra from 4000cm^{-1} to 650cm^{-1} were recorded. The peak at 2275 cm^{-1} corresponding to the cyanide group of the acrylonitrile was used as reference for all ABS spectra. For polystyrene and poly (methylmethacrylate) spectra, peaks at 1600cm^{-1} and 3000 cm^{-1} were used as references respectively.

The growth or decay of monitored absorption peaks were expressed as indices.

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The indices are defined as the ratio of the absorbance of the growing or decaying peaks to that of the reference peak.

In following the chemical changes occurring during degradation of the polymers the main bands monitored are the increasing carbonyl absorbance abound 1725cm^{-1}, the increasing hydroxyl absorbance around 3450cm^{-1} and the decreasing absorbance of the trans. 1, 4- polbutadiene at 965cm^{-1} a nd cis - 1, 2 - polybutadiene.

3.12

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C H A P T E R 4

Pages

STUDIES ON PLOYSTYRENE AND POLY(METHYLMETHACRYLATE) 32 - 46

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The stabilizing effects of 3, 5-di-t-butyl-4-hydroxybenzylthioglycollate (DBHBT) and Zincdiethyldithiocarbamate (ZnDEC) have been compared with that of a commercial phenolic antioxidant, Irganox 1076. The degradation of polystrene (PS) and poly (methylemethacrylate), PMMA, during oven aging and UV irradiation with and without the three stabilizers have been studied. Synergistic mixtures of the stabilizers have also been investigated.

In all the work now reported on PS and PMMA, a 2% level (W/W) of stabilizer concentration has been employed in all cases. This is as a result of preliminary investigations carried out in determing the optimum level of activity for these stabilizers.[1]

4.1 Results and Discussions

4.2 Thermal Degradation of PS.

The general feature of the spectra of a degraded sample of unstabilized PS is as shown in Fig. I. It can be seen that a carbonyl growth is noticeable at 1740cm^{-1} and a peak at 1680cm^{-1}, probably due to unsaturated carbonyl groups. As degradation continued, the peak at 1680cm^{-1} became a shoulder to the carbonyl peak at 1740cm^{-1}. An hydroxyl group can also be seen to develop at 3625cm^{-1}. This is perhaps an hydroperoxide hydroxyl. In this work, main interests have been placed on the growing hydroxyl group at 3625cm^{-1} and the carbonyl group at 1740cm^{-1}.

Fig. 2 shows the dependence of hydroxyl index on time of heating of stabilized and unstabilized samples. The unstabilized sample appears to be

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the least stable and degrades fastest. The unstabilized sample exhibits an induction period of 35hrs and embrittles after 540hrs. The commercial phenolic anti-oxidant, Irganox 1076 improves the stability of PS as is shown in this figure. In table I it can be seen that the induction period has been improved to 135hrs and the embrittlement time to 1160hrs.

In the presence of ZnDEC and DBHBT, the hydroxyl index can be seen to fall slightly initially. This phenomenon suggests that both ZnDEC and DBHBT act, at least in part, as peroxide decomposers, Hydroxyl groups which are present are converted to peroxide which are consumed by the sulphide group of these stabilizers. This behaviour is found with all samples containing either ZnDEC or DBHBT and their mixtures but absent in the samples containing Irganox 1076 alone. This might mean that ZnDEC and DBHBT act by a similar mechanism but differently to Irganox 1076 in their stabilization of PS.

Table I shows that DBHBT is the best thermal stabilizer.

The shapes of the plots of the carbonyl index with heating time (Fig. 3) is quite similar except for the different time of induction. Fig. 3 shows that the induction periods observed for the appearance of the carbonyl groups correspond with those for hydroxyl groups. This may suggest that hydroxyl and carbonyl groups are probably formed simultaneously from the degradation reaction.

.3 Synergistic Mixtures

Obviously, the most important and technologically useful aspect of any

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work of this nature is finding a combination of stabilizers which will give rise to synergism. In this work, two-component combinations of the three stabilizers have been used and the results obtained are now discussed below.

Fig. 4 shows the dependence of hydroxyl index upon heating time for three stabilizer combinations. The table below illustrates the results obtained.

Stabilizer Combination	I. P. Obtained	I.P. on additive basis,
No additive	35	-
Irganox 1076 + ZnDEC	405	315
Irganox 1076 + DBHBT	365	340
ZnDEC + DBHBT	615	305

It is evident from the table that the formulation of ZnDEC + DBHBT is the best synergist of the combinations. The combination of Irganox 1076 and ZnDEC also shows good synergistic activity. On the other hand the behaviour of Irganox 1076 and DBHBT together each of which is a good thermal stabilizer is not as good as perhaps may be expected. The reason for this behaviour is not fully known but this will be discussed later when the stabilizing activity of these stabilizers are looked at more critically. Presently, it thus appear that the activity of the combination of Irganox 1076 and DBHBT is probably additive.

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Unlike the curve of the unstabilized sample, the other curves indicate an initial fall in the hydroxyl level. This observation agrees with the earlier result that ZuDBC and DBHBT individually behaved as peroxide decomposing stabilizer and further suggests that the individual behaviours are still maintained in the mixtures.

Fig. 5 shows the dependence of carbonyl index on heating time in the presence of mixtures of stabilizers. It is seen here that the ZuDBC - DBHBT combination is the best synergistic mixture and the slope of the post - induction portion of the curve is smallest. This shows that the synergistic mixture is not only good in protecting PS against thermal degradation for a long period of time, but also that the rate of degradation after induction is slowest. It was also observed that the least colour developed in this sample during exposure.

4 Photo - Degradation of PS.

The dependence of the hydroxyl and carbonyl groups on ultra-violet irradiation of PS samples are shown in Figs. 6 - 9.

It can be seen in fig. 6 that the conventional antioxidant, Irganox 1076 still imparts some stability to PS under UV irradiation. It has been shown that both thermal and photo-degradation of PS follow a free radical mechanism.[23] Therefore, even though Irganox 1076 is not classified as a UV stabilizer, it can still impart stability during UV irradiation

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by interacting with free radicals and thereby terminating chain reactions. The peroxide decomposing nature of ZnDEC and DBHBT is still observable during UV irradiation as depicted by the slight fall in hydroxyl index of the samples containing the two stabilizers.

The UV stabilizing activity of ZnDEC and DBHBT may be attributable to sulphur products in part and to some energy transfer process, particularly, in the case of ZnDEC.

Results of the synergistic mixtures are represented by figs 8 and 9. The unstabilized sample has an induction period of 50hrs and embrittlement time of 630hrs while in the presence of Irganox 1076 and DBHBT the times are increased to 355 and 1685hrs respectively. This is an improvent of about 7 times in the induction period and about 3 times in the embrittlement properties. The combination of Irganox 1076 and ZnDEC has been found to be a better synergistic mixture than the combination of Irganox 1076 - DBHBT. Both the induction period and embrittlement time have been greatly improved by the former mixture. As was found under thermal degradation, the ZnDEC - DBHBT mixture exhibits the greatest synergistic activity under UV irradiation, This mixture has extended the service time of the sample 4 times and improved the induction period over 13 times. The times to embrittlement and periods of induction have been presented in table. II

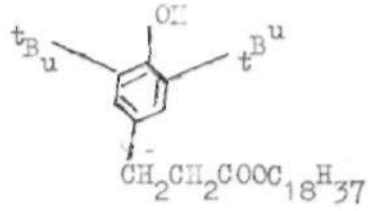
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Table II: Induction Periods and Embrittlement Times (in hours)

Material	Thermal		UV	
	I.P	E.T	I.P	E.T
Unstabilized PS	35	540	50	630
PS + Irganox 1076	135	1160	124	1342
PS + ZnDEC	180	1350	180	1492
PS + DBHBT	205	1584	165	1665
PS + (Irganox 1076 + ZnDEC)	405	1800	440	2224
PS + (Irganox 1076 + DBHBT)	365	1656	355	1920
PS + (ZnDEC + DBHBT)	615	2412	660	2452

4.5 Comments on the Stabilizing activity of Stabilizers.

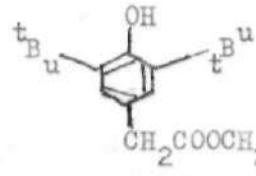
The structures of the stabilizers are presumed to be important in the stabilization of the compounds and the structures have been given below.



Irganox 1076



ZnDEC



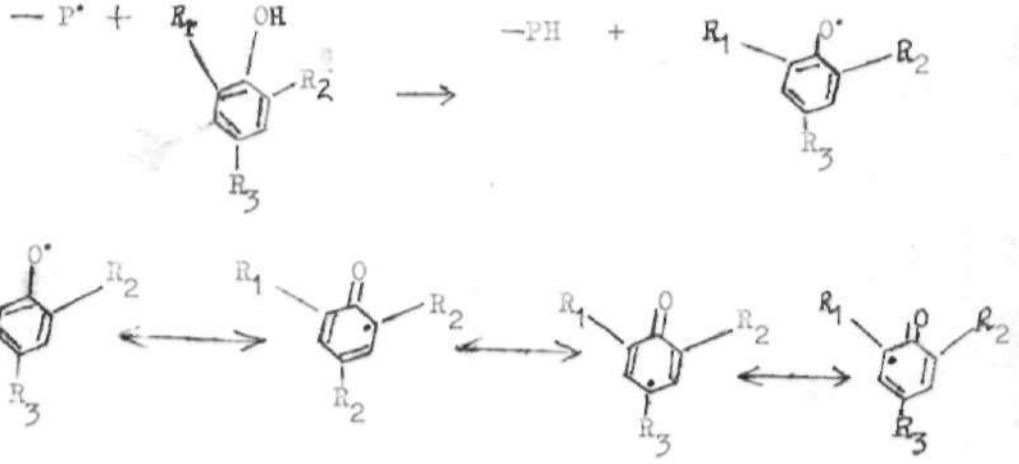
DBHBT

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The antioxidant, Irganox 1076 is believed to act in interrupting the chain reactions by combining with the propagating free - radical species and thus forming non-reactive (stable) products. It acts by the mechanism

$$-P^{\bullet} + AH \longrightarrow -PH + A^{\bullet} \quad \text{(Stable radical)}$$

The lack of activity of the reaction product derives from the resonance stabilization and/or dimerization with other species.



On the basis of the autooxidative chain process, the antioxidant operates by a radical chain breaking mechanism by removing from the medium the two important species normally involved in the chain propagation step, i.e. alkylperoxy and alkyl radicals.

From the structures of the stabilizers it can be seen that both Irganox 1076 and DBHBT should behave as good antioxidant by this chain breaking mechanism.

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In addition to its ability to act as a radical chain breaking antioxidant through its phenol group and resonance stabilization, DBHBT is also capable of acting as a peroxide decomposer. DBHBT may remove peroxide radicals and decompose hydroperoxides as they are formed as in reactions below.

$$>CHOO^{\cdot} + RSH \longrightarrow >CHOOH + RS^{\cdot}$$

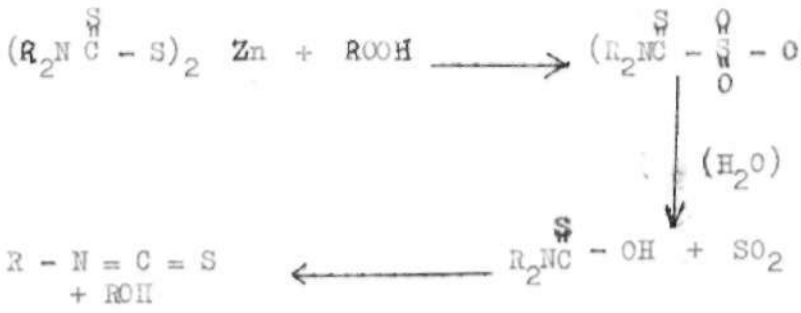
$$>CHOO^{\cdot} + RS^{\cdot} \longrightarrow >CH\text{-}OOSR \text{ (Stable products)}$$

In effect, it means that DBHBT is able to act both as a primary and a secondary stabiliser. This may perhaps explain why it behaves as a very good thermal stabilizer.

Nickel compounds have been found to interact with photo - excited molecules deactivating them by dissipating the excess energy as IR radiations.[4], Briggs and Nickellar[5] have also found that the effectiveness of a series of nickel complexes as UV stabilizers for polypropylene is similar to their quenching ability for anthracene i.e. UV light is absorbed by the highly conjugated structure and dissipated as harmless IR radiation by a resonance stabilization mechanism. Chakraborty and Scott[6] also showed that the effectiveness of nickeldialkylthiocarbamates as UV stabilizers is a function of their role as catalysts for the non - radical decomposition of hydroperoxides and that Irganox 1076 synergises with NiDBC as a thermal stabilizer.

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The action of ZnDMC in the present work is thought to be due to a combination of its ability to decompose peroxides, direct absorption of UV light and quenching of polymer excited states by the energy transfer mechanism. The ability of ZnDMC to decompose hydroperoxides in a non-radical mechanism may be represented by the following reactions.



Synergism is presumed to arise since inhibition can be affected at different stages in the oxidative reaction. Therefore combinations which suppress oxidation at different stages are particularly effective. A chain terminator suppresses the rate of initiation, but, as each oxidative chain is terminated, a molecule of peroxide is formed. Decomposition of peroxides which would yield radicals and make the reaction autocatalytic is prevented in the presence of a peroxide deactivator. In this way, additional radicals are not formed and the chain terminator is preserved thus yielding excellent stabilization.

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The activities of [illegible]C and DBHBf may also be enhanced because they could act as a reservoir of potentially available sulphur oxides which could act as powerful antioxidants and also imparting some UV stability. This phenomenon is supported by the work of Amin and Scott[7] who discovered that Zinc, nickel and cobalt complexes are relatively stable to oxidative treatment at high temperatures and that the process leading to their destruction involves reaction with hydroperoxides and the products formed, notably SO_2/SO_3 are powerful antioxidants. Because chain-breaking and peroxide decomposing stabilizers interfere at different points in the auto-oxidation process, they mutually reinforce one another leading to an effect greator than the sum of the effects of each stabilizer alone. This is synergism.

As well as being complementary in mechanism, the two classes of anti-oxidants frequently complement each other in their response to enviromental conditions thereby giving rise to protection over a broader period of time and wider range of enviromental conditions than either type above.

4.6 Poly (methylmethacrylate)

Fig. 10 shows the i. r. spectra of oven aged sample of PMMA. Similar spectra have been obtained for UV irradiated samples. Only the

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hydroxyl indices were monitored for all investigations of PMMA. It can be seen that two hydroxyl peaks developed; one at 3450cm^{-1} and the other at 3650cm^{-1}. The former band is believed to arise from hydrogen bonded hydroxyl group, probably due to adsorption of moisture at the film surface while the band at 3650cm^{-1} is an hydroperoxide hydroxyl group. The calculated indices have been based on the hydroxyl group at 3650cm^{-1} which is been to grow with increased heating time.

4.7 Thermal degradation of PMMA

Fig. 11 shows the dependence of hydroxyl index on oven ageing in the presence of Irganox 1076, ZnDEC and DBHBT while fig. 12 shows the same parameters but in the presence of mixtures of stabilizers. The initial fall in the concentration of the hydroxyl group observed with PS has been found in all cases studied with PMMA. This evidence may suggest that during thermal processing of PMMA, some hydroperoxides or other hydroxyl groups are incorporated. When incorporated individually, the efficiency of the stabilizera for PMMA under oven ageing has been found in the order.

Irganox 1076 < ZnDEC < DBHBT. The unstabilised sample has an induction period of 25hrs and embrittlement time of 340hrs. Table II shows

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the improvements brought about on the embrittlement properties and induction periods by the incorporation of the stabilizers.

Table III: Induction Periods and Embrittlement Times (in hrs)

Material	Thermal		UV	
	I.P	E.T	I.P	E.T
Unstabilized PMMA	25	340	15	280
PMMA + Irganox 1076	130	960	115	792
PMMA + ZnDEC	158	1200	148	980
PMMA + DBHBT	174	1505	134	955
PMMA + (Irganox 1076 + ZnDEC)	385	1722	334	1135
PMMA +(Irganox 1076 + DBHBT)	342	1624	300	1070
PMMA + (ZnDEC + DBHBT)	430	1884	395	1492

Fig. 12 shows the effect of mixtures of stabilizers on the oven ageing of PMMA. The greatest stabilization is obtained with the ZnDEC-DBHBT system and the least from Irganox - DBHBT. This result is surprising given the fact that DBHBT behaves better than ZnDEC as a thermal

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Fig. 15 compares the degradation under UV irradiation with that under oven ageing for unstabilised samples. It is evident from this plot that PMMA degrades faster when irradiated with UV light of 254nm that when heated in air oven thermostatted at 100°C. This means that PMMA is more stable to heat at the given temperature than to UV light.

4.9 Conclusion.

From the results of the investigations with PS and PMMA, it can be concluded that under UV irradiation, the relative effectiveness of the stabilizers employed is in the order, ZnDEC > DBHBT > Irganox 1076. On the other hand, as thermal stabilizers the increasing order of effectiveness is Irganox 1076 < ZnDEC < DBHBT. Since Irganox 1076 is used commercially as a thermal stabilizer, the use of DBHBT as a substitute is highly recommended.

A two - component stabilizer of ZnDEC and DBHBT performs much better thermally and should be preferred to DBHBT alone. For both thermal degradation and UV irradiation, a synergistic mixture of ZnDEC DBHBT is an effective stabiliser.

The results obtained here are comparable with those of Kolawole[C] on BHBM. DBHBT is an ester of BHBM. BHBM is both difficult to prepare

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and the yield is low. On the other hand ester, DBABT, is easier to prepare and has a higher yield. It is therefore advantageous, economically, to substitute BHBM with DBABT as a thermal stabilizer.

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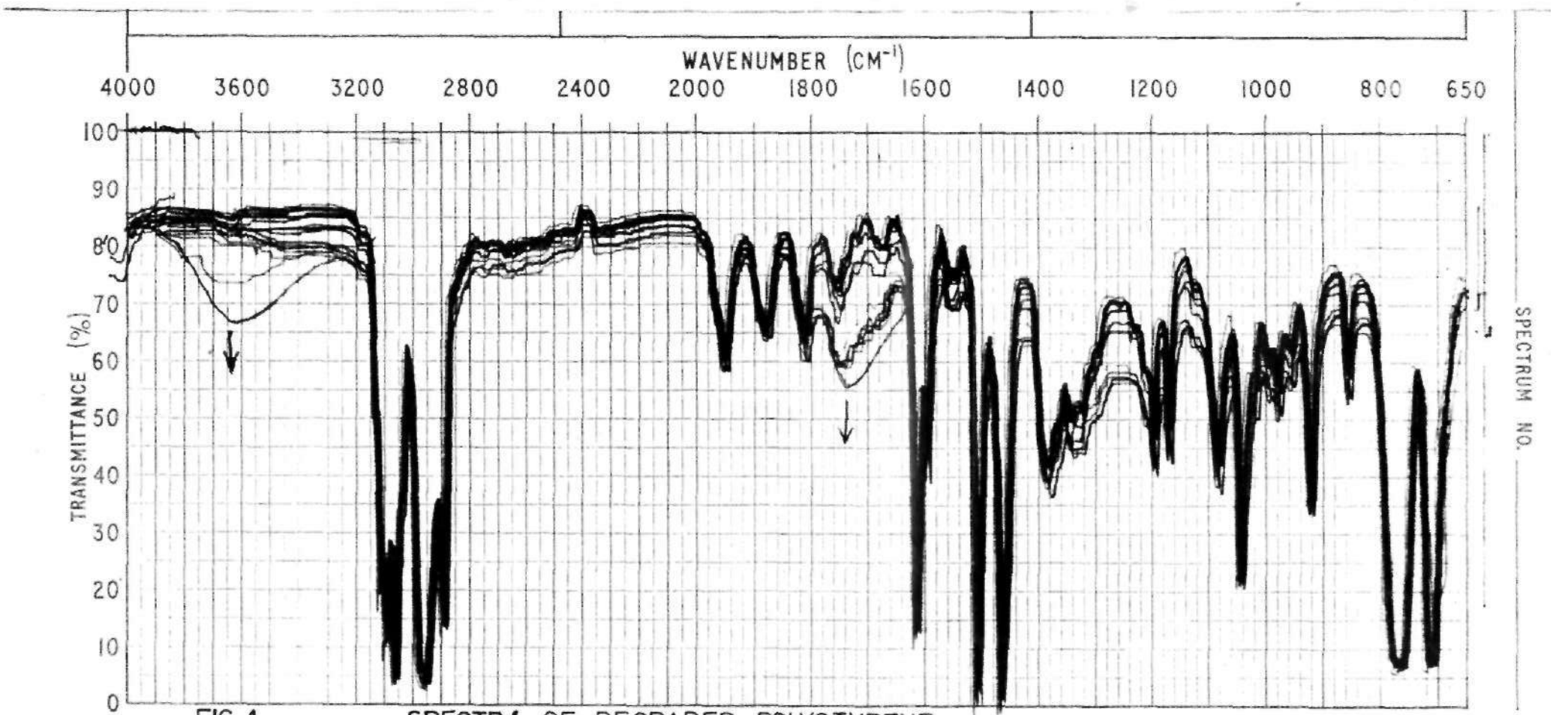


FIG. 1 SPECTRA OF DEGRADED POLYSTYRENE

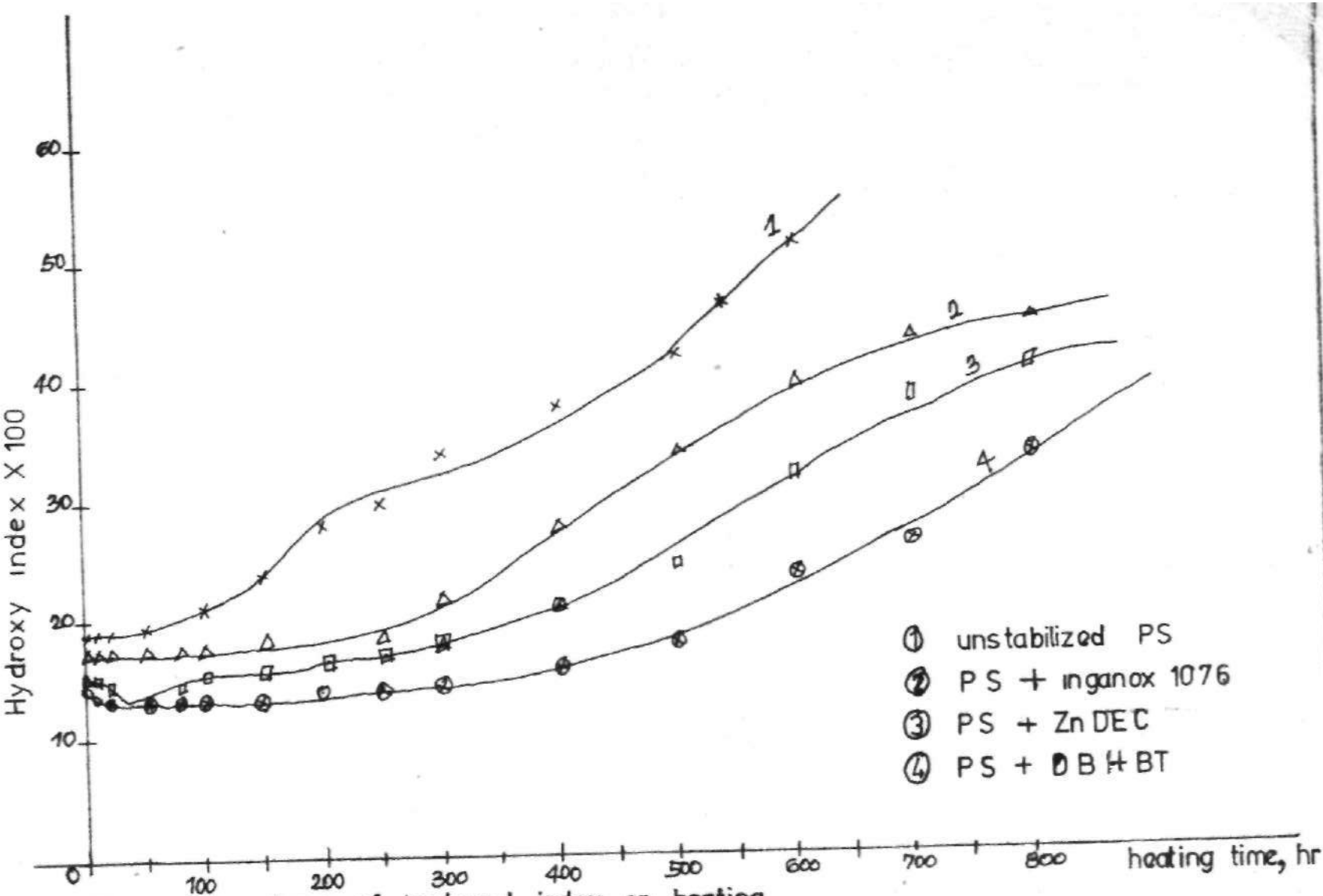


Fig 2. Dependence of hydroxyl index on heating

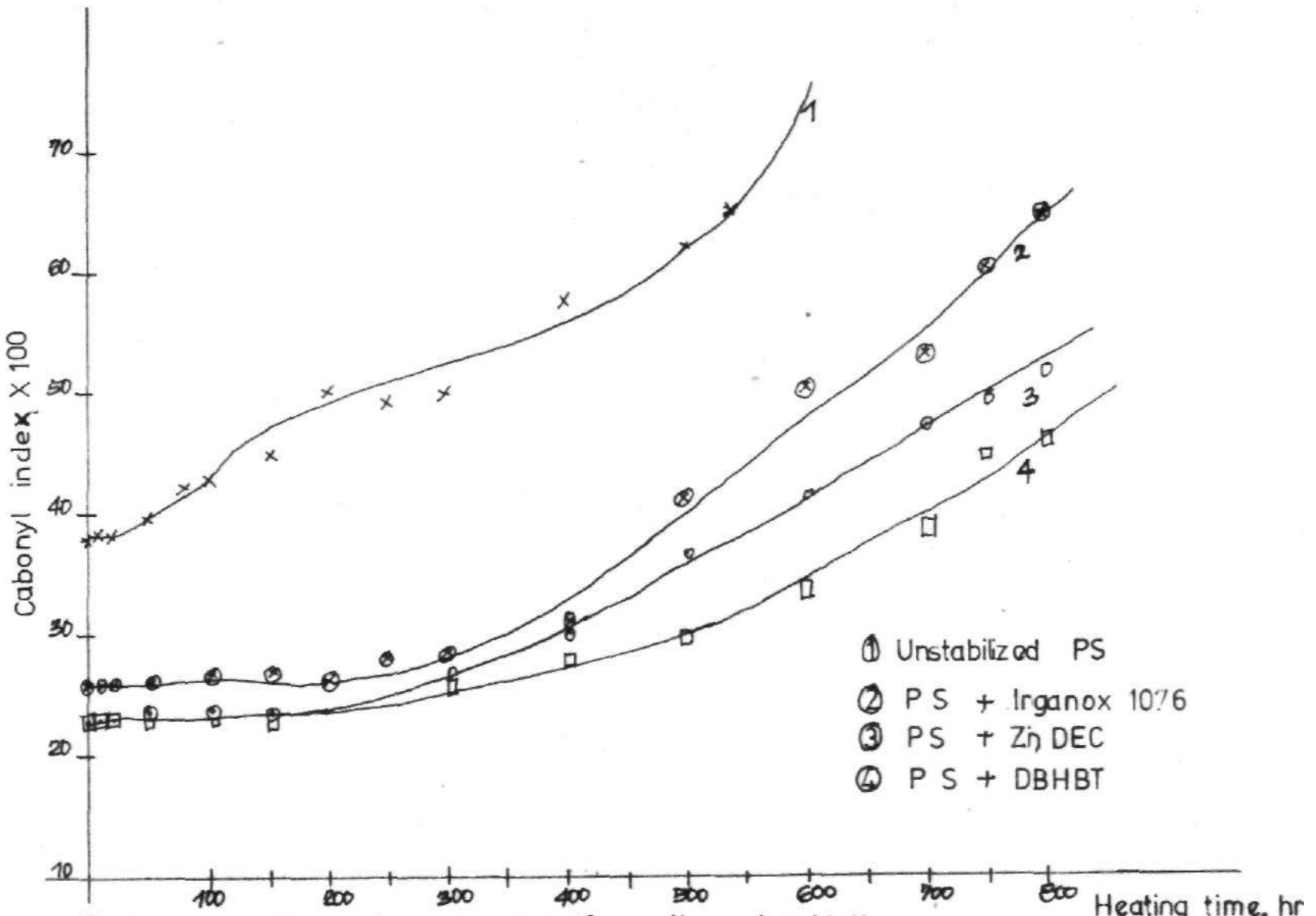


Fig 3 Dependence of Carbonyl index on thermal oxidation

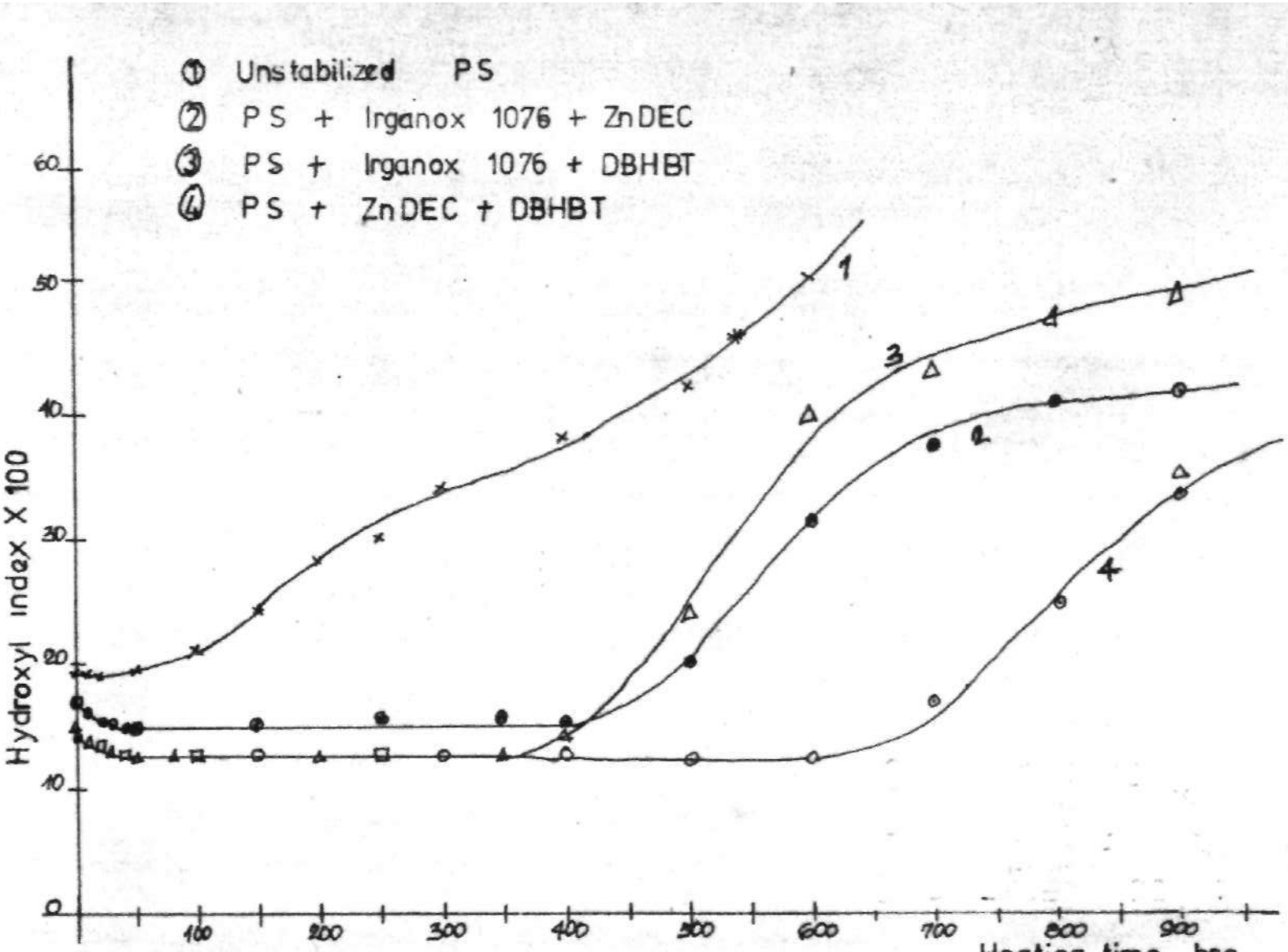


Fig 4. Dependence of hydroxyl index on thermal oxidation

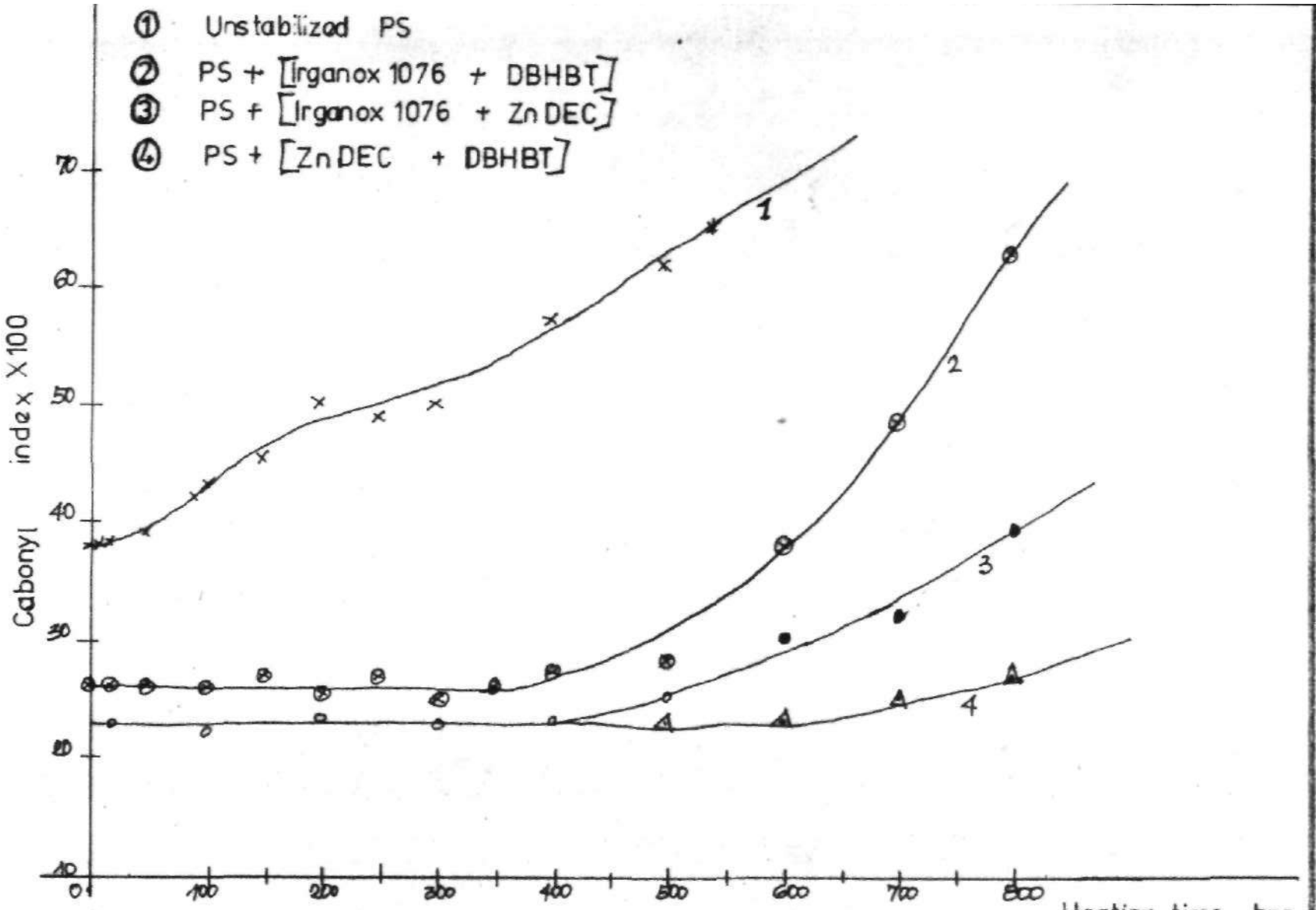


Fig 5 Dependence of Cabonyl index on heating time

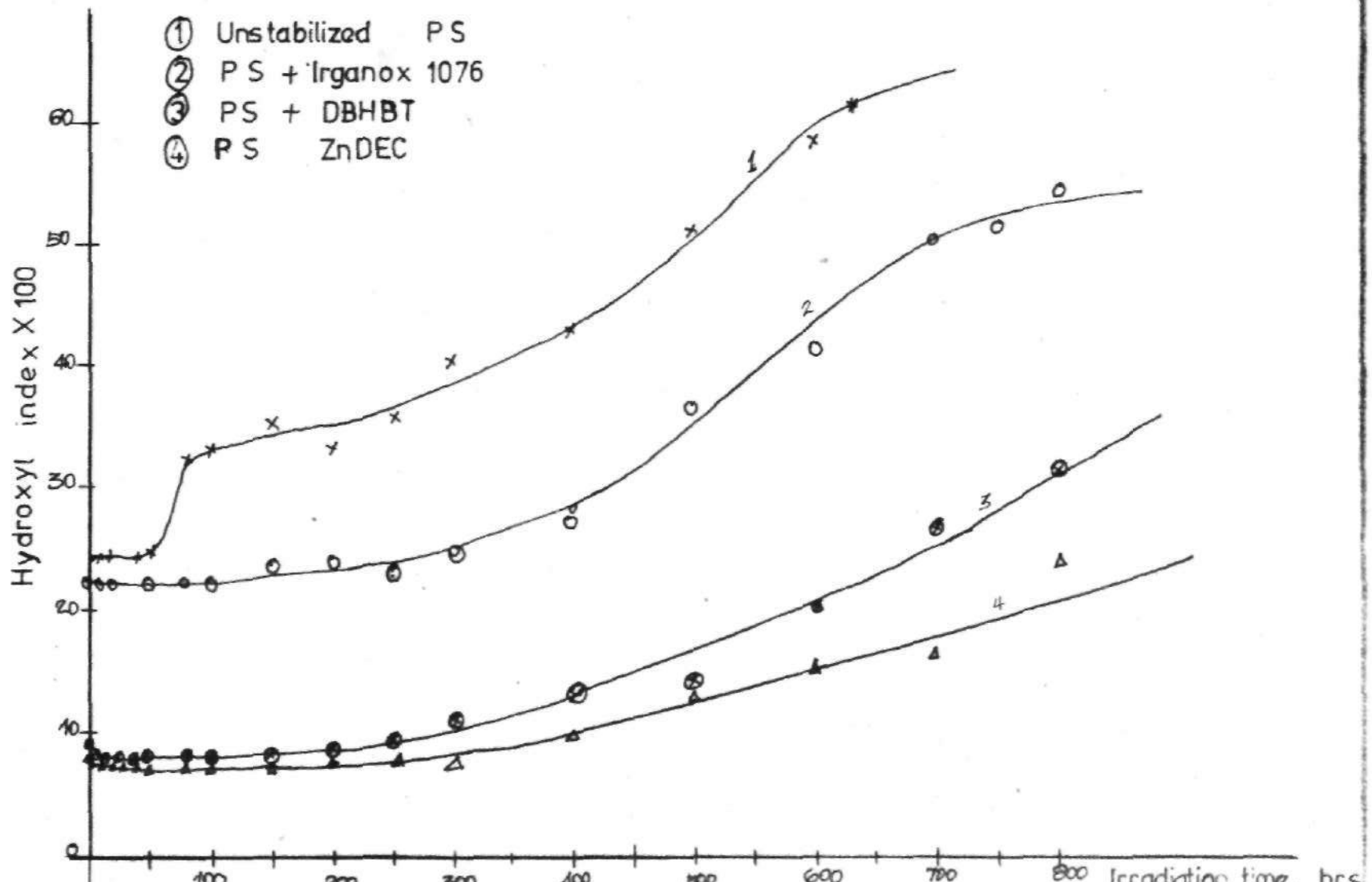


Fig6 Dependence of hydroxyl index on uv-irradiation

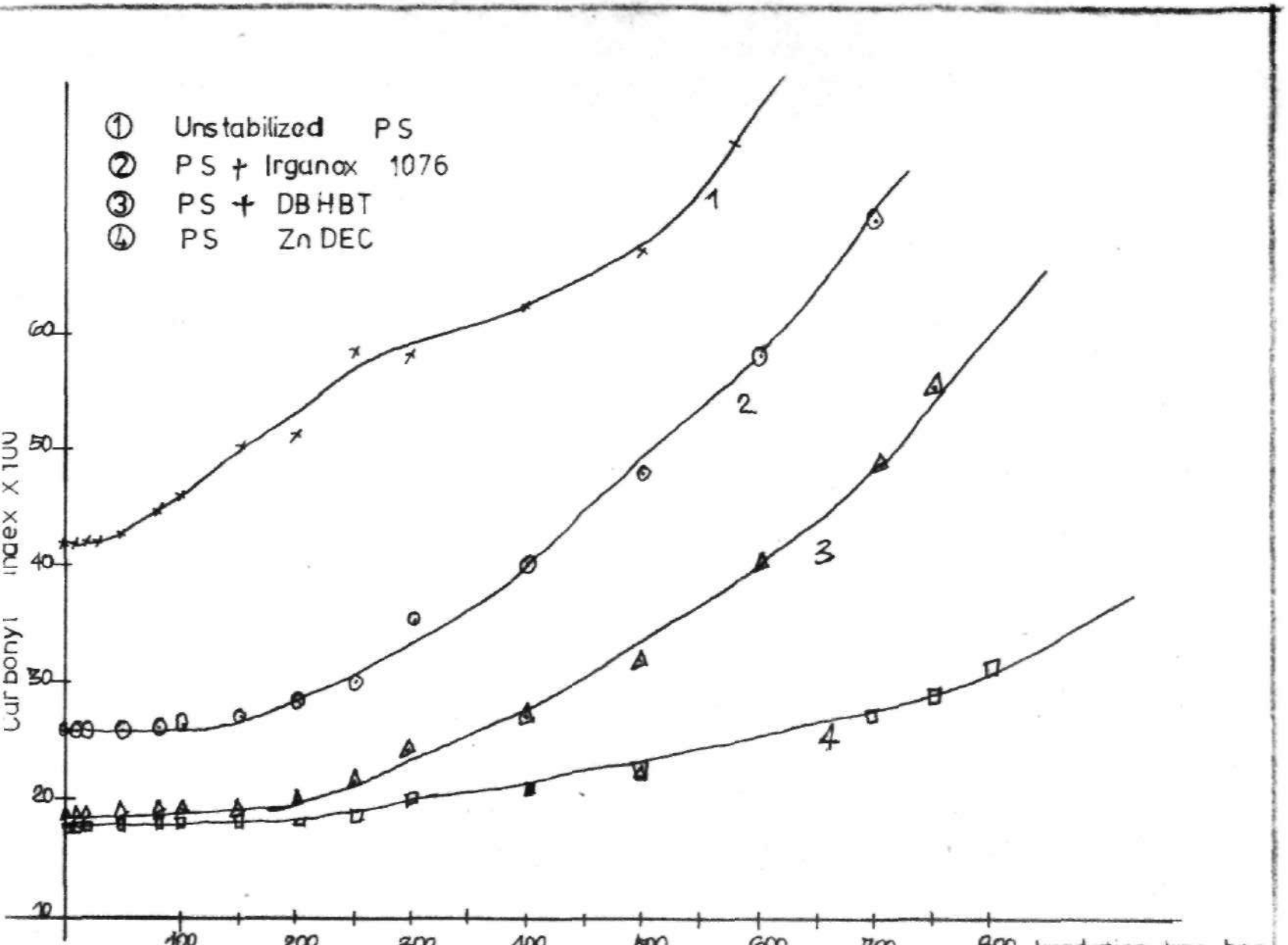


Fig 7 Dependence of Carbonyl index on uv-irradiation

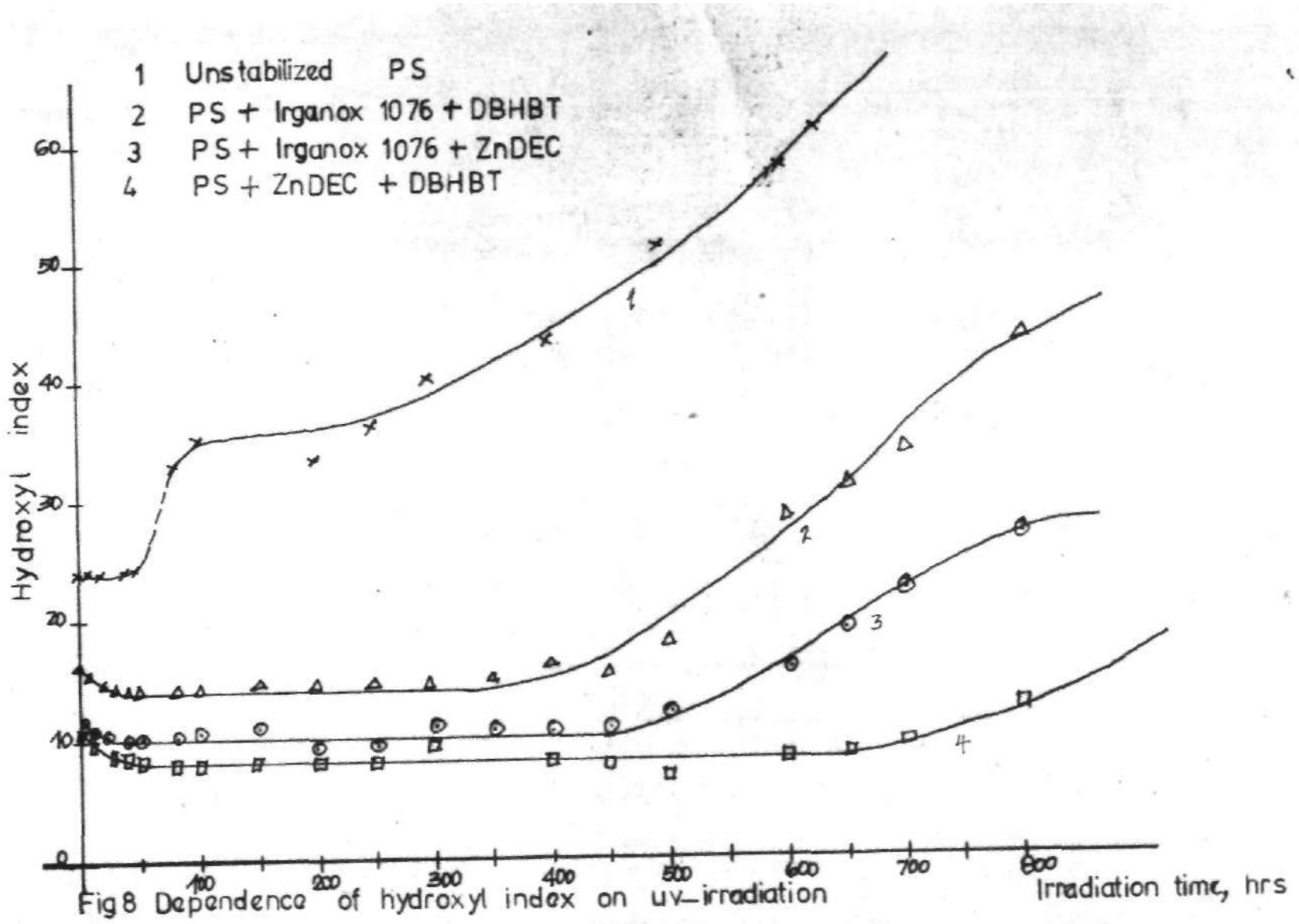


Fig 8 Dependence of hydroxyl index on uv–irradiation

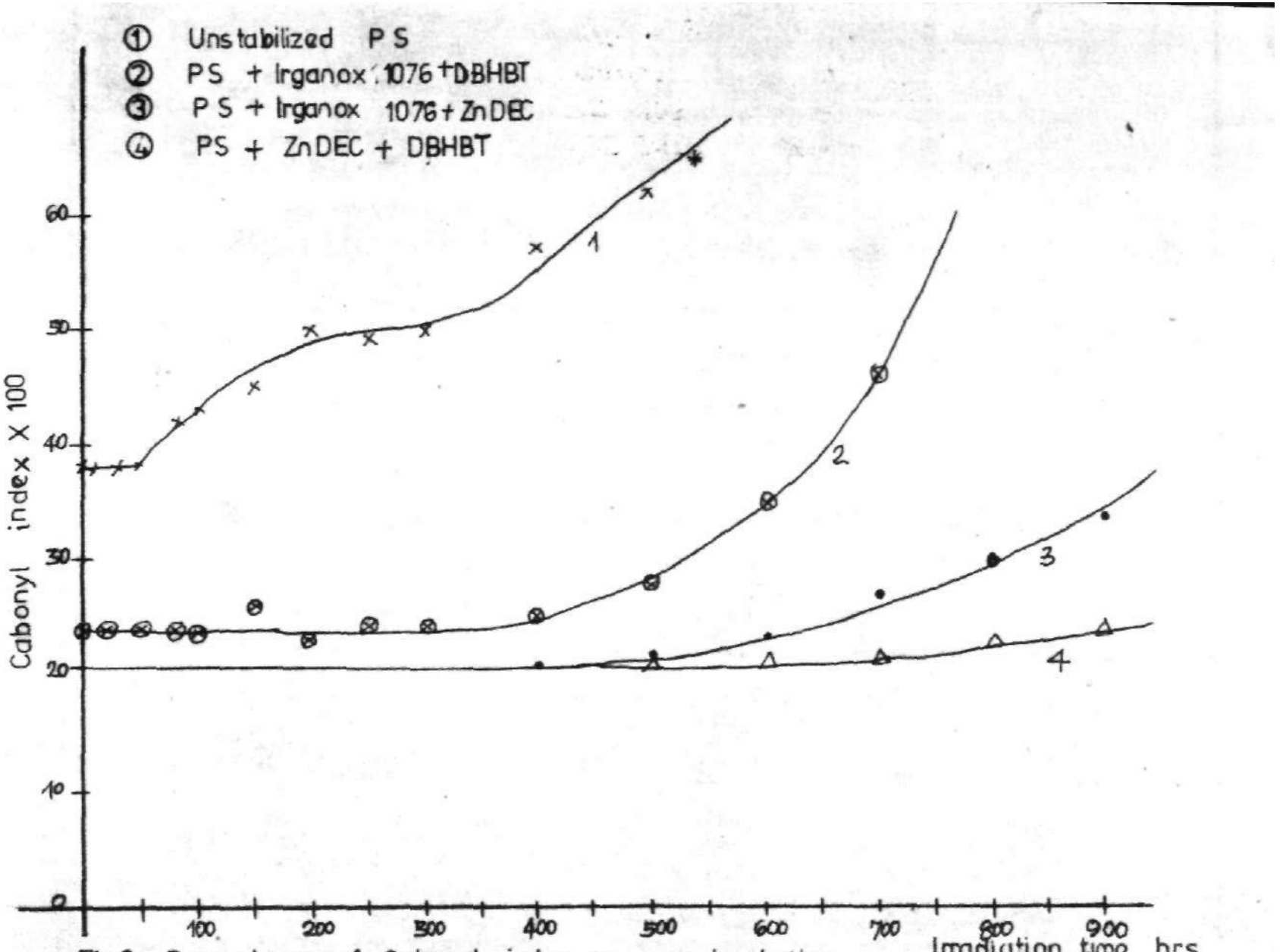


Fig 9 Dependence of Cabonyl index on uv-irradiation

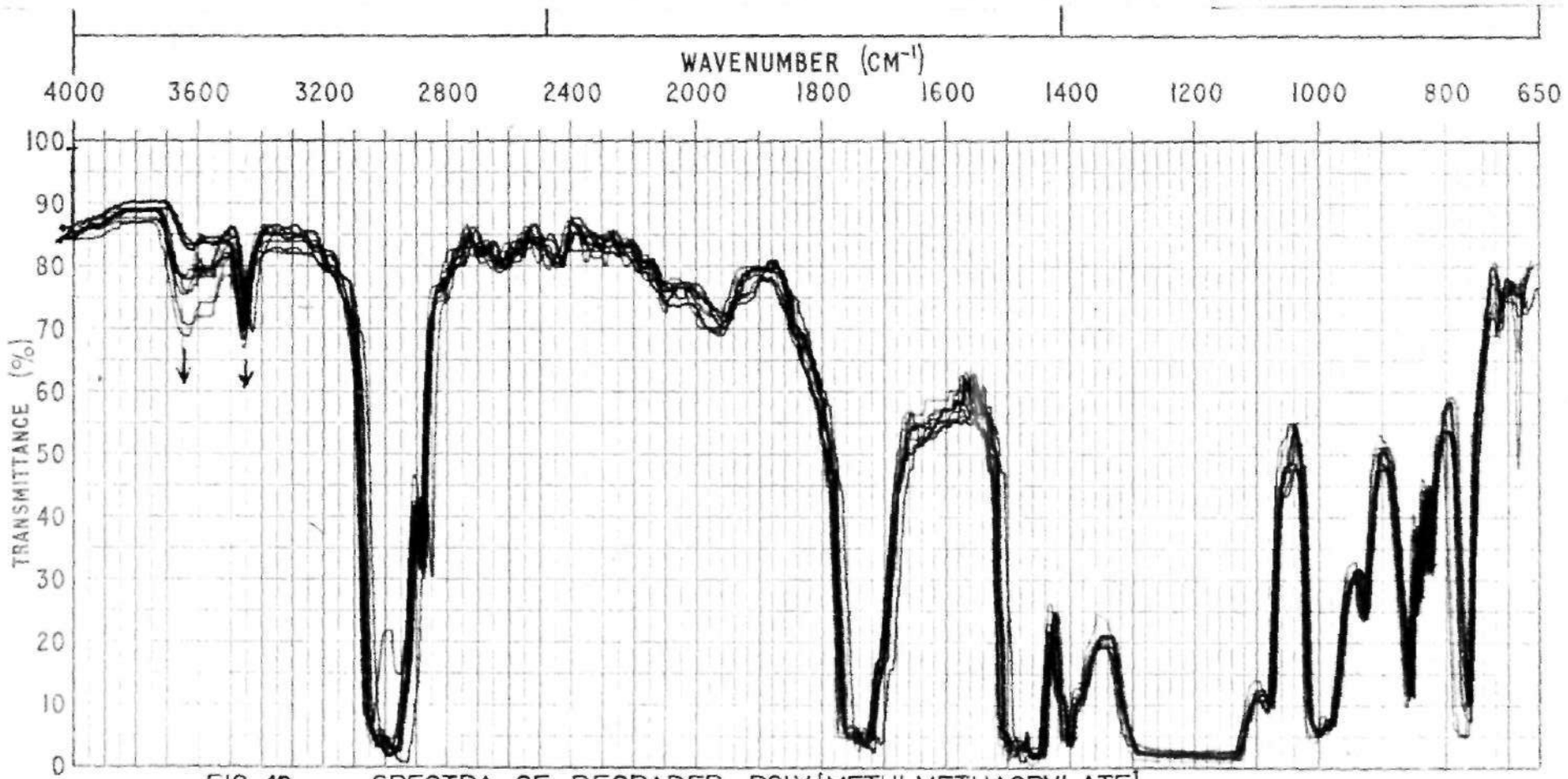


FIG. 10 SPECTRA OF DEGRADED POLY (METHLMETHACRYLATE)

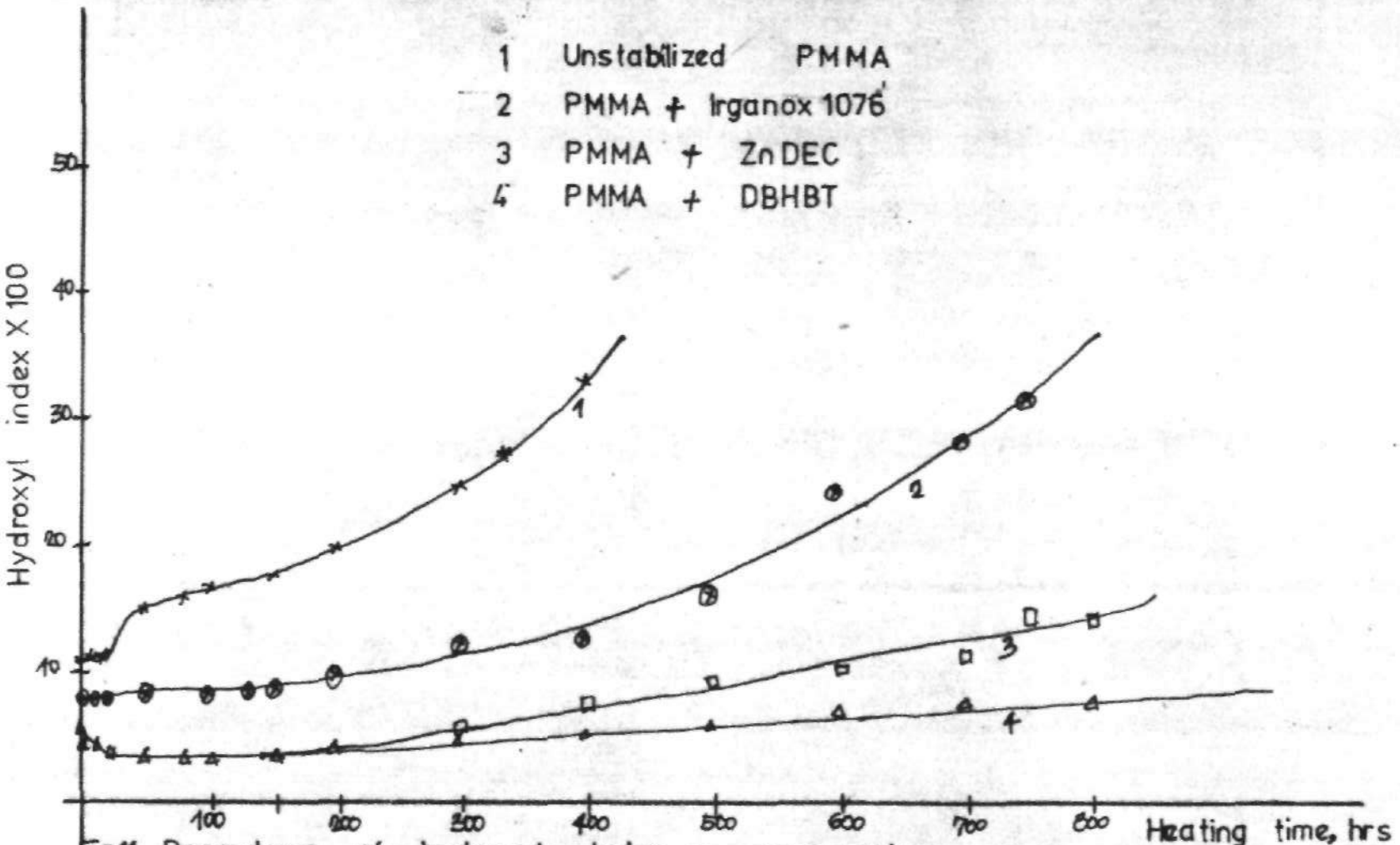


Fig 11 Dependence of hydroxyl index on oven ageing

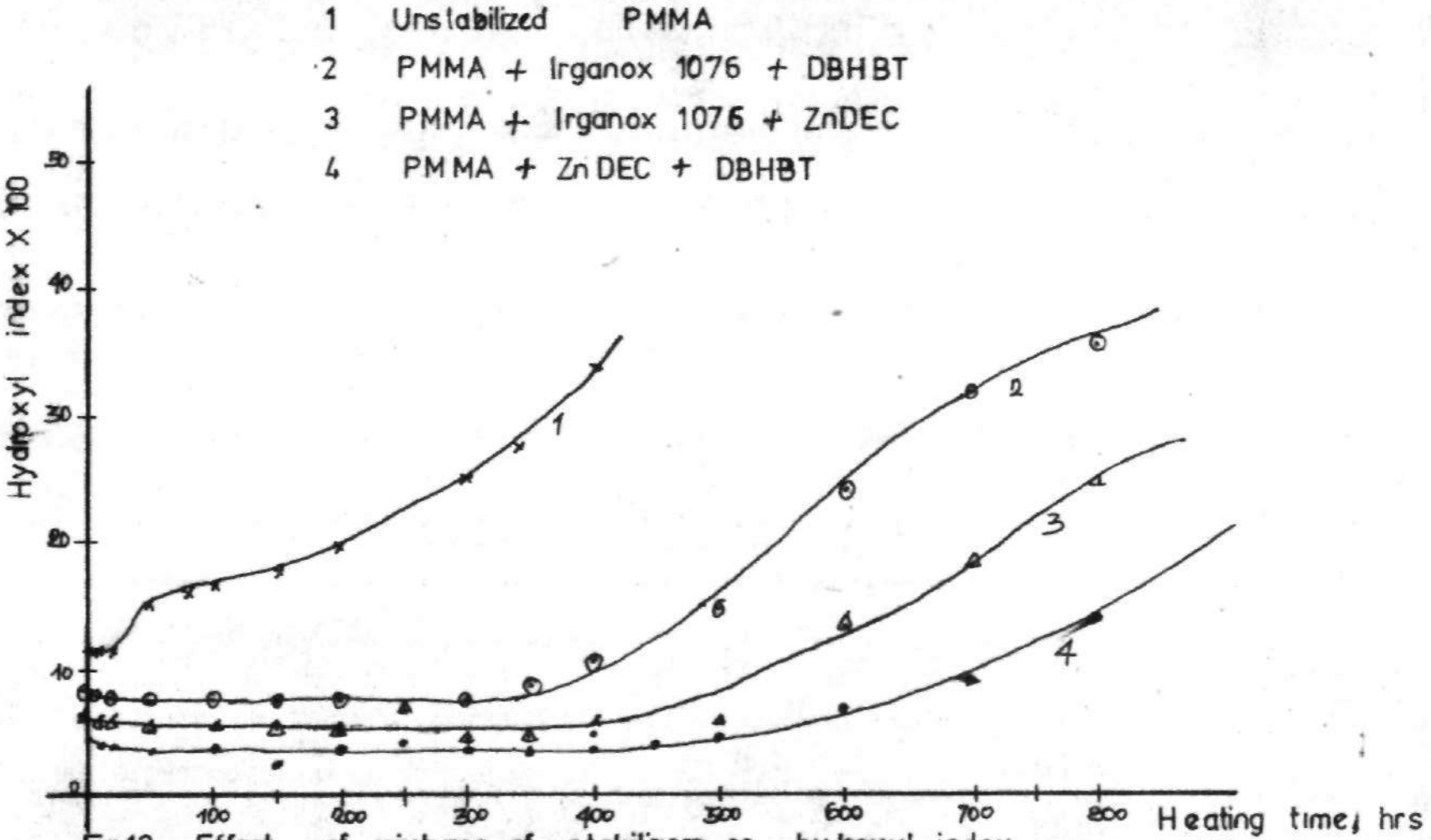


Fig 12 Effect of mixtures of stabilizers on hydroxyl index

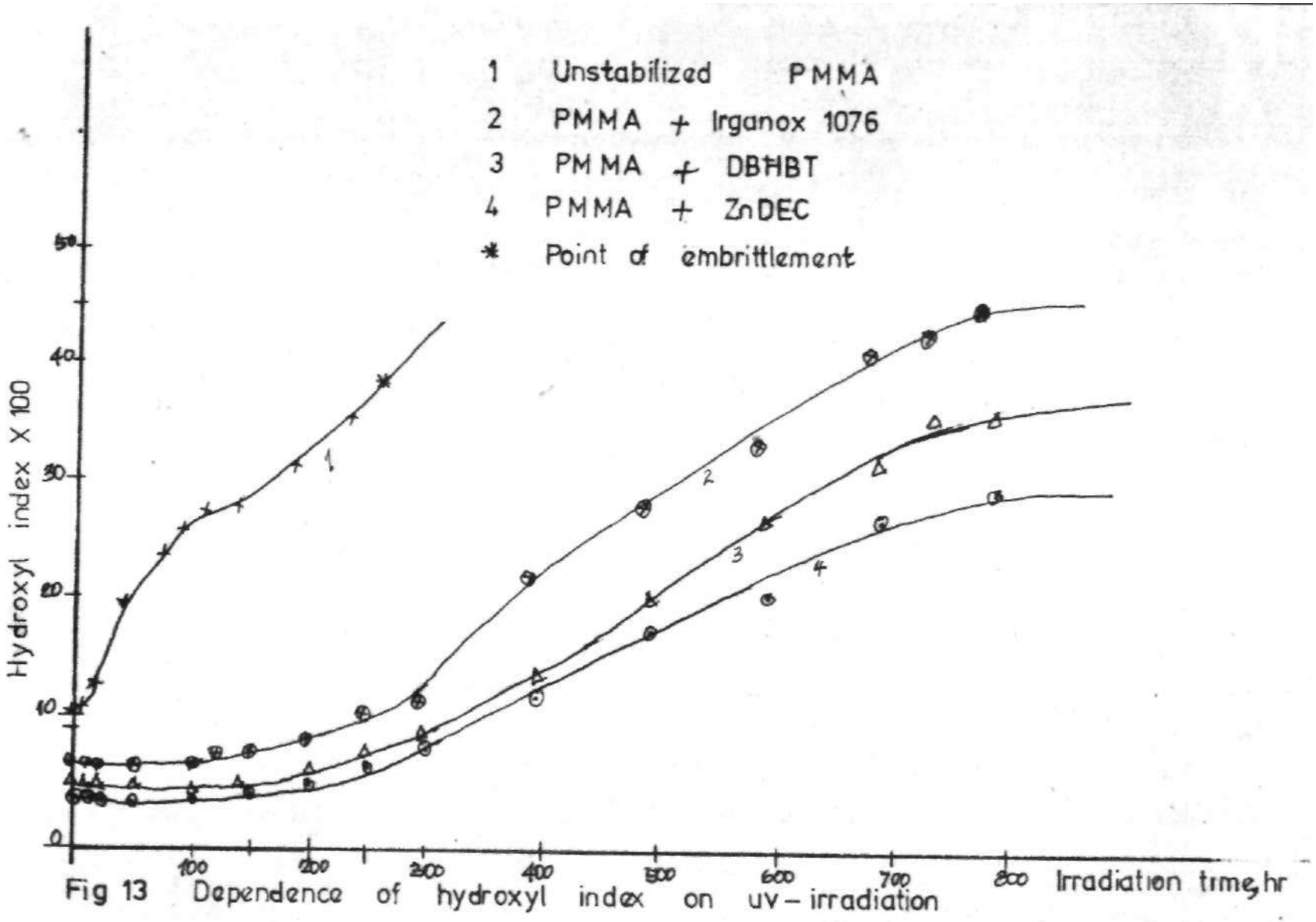


Fig 13 Dependence of hydroxyl index on uv – irradiation

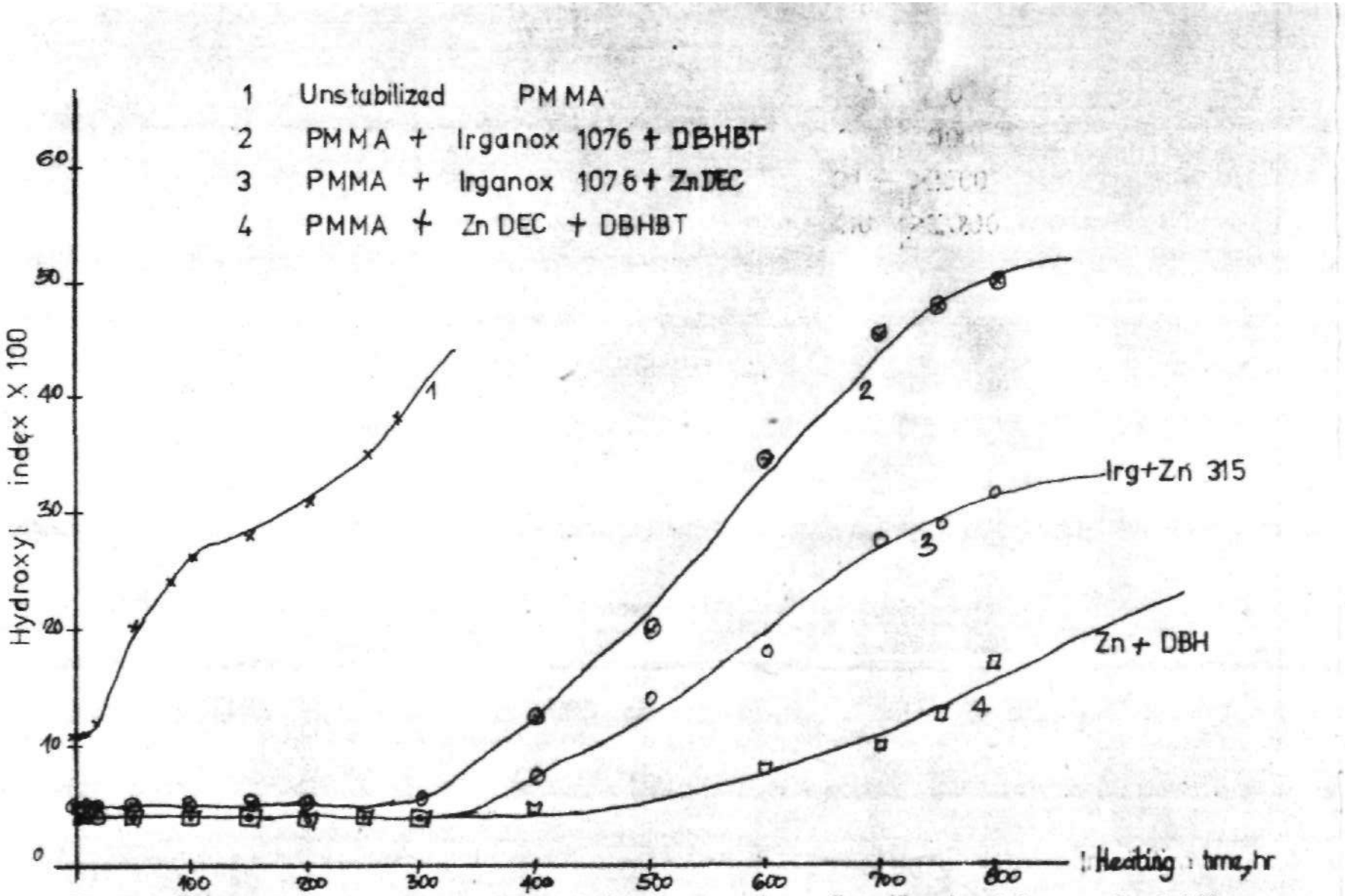


Fig 14 Effect of heating on hydroxyl index in samples with & without mixtures of stabilizers

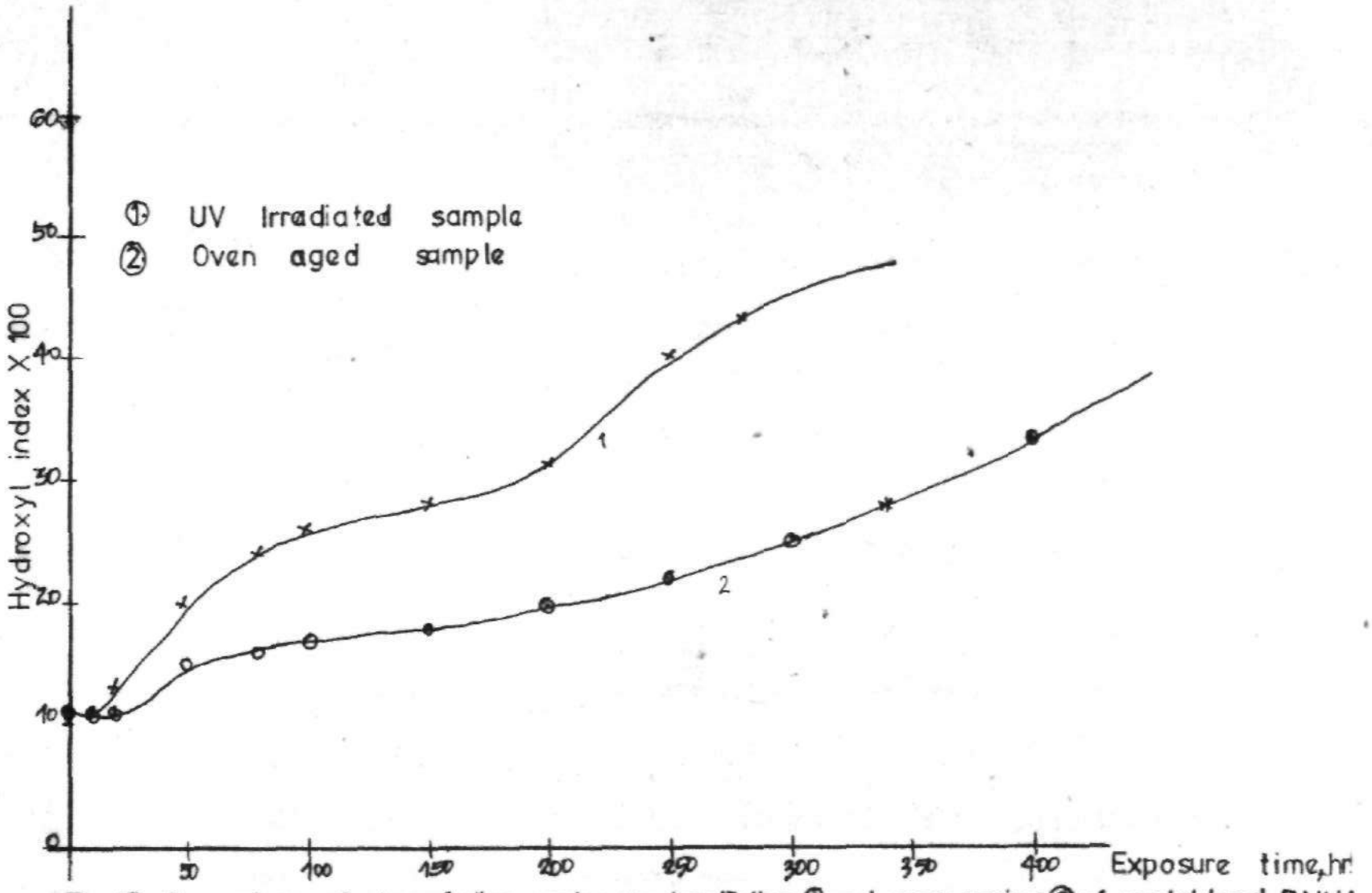


Fig 15 Comparison of degradation under uv irradiation ① and oven ageing ② of unstabilized PMMA

C H A P T E R 5

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S T U D I E S O N

ACRYLONITRILE - BUTADIENE -

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5.0 RESULTS AND DISCUSSIONS

5.1 General features of the i.r. spectra

A common feature observed is that the spectra of degraded samples exhibited growths in b nds corresponding to the carbonyl (1725cm^{-1}), the hydroxyl (around 3450cm^{-1}), polytrans - 1, 4-butadiene and polycis-1, 2-butadiene at 965 and 910cm^{-1} respectively; (Fig. 1). The double bonds at 965cm^{-1} seem to disappear faster than those at 910cm^{-1}.

Hydroxyl and carbonyl bands grew in all the spectra, but, these bands were, however, preceeded by the decay of the polybutadiene content of ABS. After a certain length of time, the polytrans - and polycis - butadiene seem to be completely destroyed as can be clearly seen in Fig. 2 The hydroxyl peak also seem to reach a maximum when the double b nds of polybutadiene are fully destroyed, while the carbonyl band continues to grow. This further growth of the carbonyl band may indicate a gradual conversion of hydroxyl to carbonyl.

In the cases of ABS samples containing some additives, the bands, exhibit an initial induction period after which the peaks at 965 and 910cm^{-1}

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diminished while those at 3450 and 1725cm^{-1} begin to grow. In ABS samples containing DDTBA, the hydroxyl bands generally decrease initially, then becoming constant before beginning to grow. This may be the case where the additive is a peroxide decomposer. Hydroxyl groups which were produced during the thermal processing are converted to peroxides which are consumed by the additive, and this inhibits degradation usually initiated by hydroperoxides. This may also explain the constancy of the carbonyl peak during this time. However, after the additive concentration level has fallen substantially, the hydroxyl concentration grows and then are converted to carbonyl which is reflected in the growing peak of the carbonyl see fig. 3. This observation seems to support the suggestion by Scott[7] that hydroperoxides photolysis is more important than carbonyl sensitisation during the initiation of photooxidation of hydrocarbon polymers.

During the ageing of the sample films, the nitrile and phenyl absorbances at 2275cm^{-1} and 1960cm^{-1} respectively, do not show any noticeable changes. This suggests that no splitting of phenyl or nitrile groups take place during degradation.

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Yellow colouration developed in the films during degradation and increased in intensity with time. This is believed to be due to the formation of carbonyl groups and the increase in intensity to the increasing level of carbonyl content. Degraded samples of ABS became insoluble in dichloromethane. This is thought to be due to the presence of cross-linked gel.

5.2 Photo - oxidation of ABS.

Fig. 2 shows the changes that occur during UV irradiation in the indices of the functional groups. Evidently, polytrans -1,4-butadiene content is much higher and also degrades faster than the polycis - 1,2-butadiene. Essentially, there appears to be no induction period in the destruction of these bands in the unstabilized ABS sample. The hydroxyl group begins to grow after two hours of induction. The carbonyl peak appears shortly after some hydroxyl has been formed. It appears from the graph that the hydroxyl group grows faster initially than the carbonyl group. That the carbonyl formation is slower than and also preceeded by the appearance of the hydroxyl group may suggest that carbonyl compounds are secondary breakdown products of hydroperoxides.

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The growing hydroxyl band reaches a maximum at about the time when the polybutadiene unsaturation is completely destroyed. This is, perhaps, an indication that the center of attack of the chain is the - C = C - and that oxidative reactions thus initiated lead to hydroxyl containing products; most probably, hydroperoxides. The decrease in the hydroxyl group afterwards points to its conversion to carbonyl groups.

5.3 Effects of Tinuvin P and DBHBT on the degradation of ABS

Fig. 4 shows the effects of two different stabilizers, DBHBT and Tinuvin P on UV irradiation of ABS and the resulting destruction of unsaturation.

Expectedly, the unstabilized sample degrades fastest; apparently without any induction period. This is an evidence of the poor weatherability of unstabilized ABS under conditions of ultraviolet irradiation. The sample containing DBHBT shows an induction period of only about 16hrs. while in the presence of Tinuvin P, the sample exhibits an induction period of 815hrs. (see table I). Evidently, this means that Tinuvin P is a good UV stabilizer while DBHBT is a poor one. Despite its poor initial UV stabilization, the post - induction period slope of the curve for DBHBT may be of interest. This slope is less sharp than the one of

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the unstabilized sample. This observation may suggest that DBHBT imparts some UV stability during this stage of ABS degradation. This may probably be due to some oxidative sulphur products from DBHBT such as SO_2, SO_3 and perhaps H_2SO_4.

Fig. 5 is a first order plot showing the effect of UV irradiation on functional groups in samples with and without Tinurin P. Similar plots have been obtained with samples containing DBHBT. For the growing bands of -OH and >C = O, $\log (A_\infty - A_t / A_\infty - A_o)$ is plotted against time of exposure where A_∞ is the maximum absorbance and A_t is the absorbance at any time t. A_o is the absorbance of the initial peak. For the diminishing band of - C = C - $\log (A_t / A_o)$ has been plotted against time of exposure where A_o is the maximum ~~absorbance (initial)~~ and A_t is the ~~absorbance~~ at any time t.

The straight lines obtained after an initial period suggest that the photo-oxidation of ABS is a process of the first order. The rate of formation of hydroxyl groups is essentially similar to the rate of destruction of double bands as may be seen from the values of the rate constants shown below.

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Additive	K values (in $10^{-6} sec^{-1}$)		
	- C = C -	- O - H	C = O
None	8.689	8.668	5.331
Tinuvin P	13.690	12.084	7.677
DBHBT	3.554	3.485	2.559

This means that photo-oxidation of ABS starts with the destruction of double bands resulting in an initial fast formation of hydroxyl. The carbonyl seems to be formed later through further oxidation of the hydroxyl. The rate of carbonyl formation is smaller than the rate of hydroxyl formation as is borne out by the rate constants. The plots for samples containing DBHBT are shown in Fig. 6. and rate constants also presented in the table above

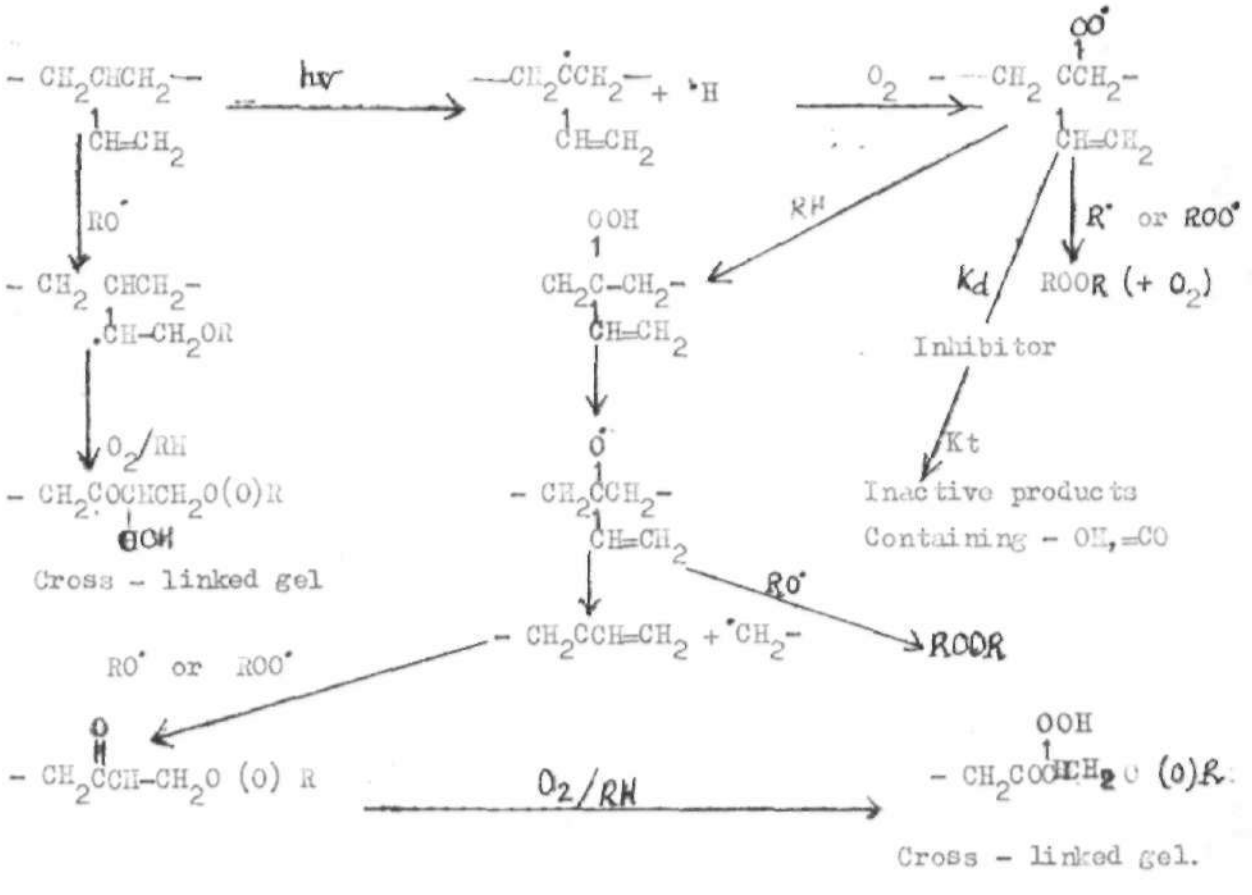
Fig. 7 demonstrates the effect of varying stabilizer concentration on the stability of ABS . It is clearly observed that even at 0.25% level, Tinuvin P imparts substantial stability over the unstabilized sample. The most economical level of application appears to be 1%.

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At a higher concentration level of 2%, the length of induction period is about same as that of 1% i.e. 315hrs. It is therefore technologically unnecessary to incerporate Tinuvin P at a higher concentration level above 1% since the induction time has not been increased.

5.4 Proposed Mechanism of ABS degradation

From the results discussed above, a photo-oxidative degradation scheme is proposed as follows.



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From the results of this work and the proposed scheme, the following may be concluded about the photodegradation of ABS.

1. The rubber segment is the initial point of photolytic attack yielding free radicals.
2. The free radicals rapidly combine with oxygen to form peroxides
3. The peroxides so formed are converted to hydroperoxides.
4. Hydroperoxides act as photoactivators for photo-oxidation.
5. Photolysis of hydroperoxides leads to cross-linking of the rubber component by addition of alkoxy radicals to 1, 2 - PB group and conjugated carbonyl formed by alkoxy radical break-down.
6. It is this cross-linking that is responsible for the insolubility of degraded sample of ABS in dichloromethane and some other solvents. and that destroys the elastomeric properties of the rubber phase.
7. Tinuvin P is a very good UV stabilizer for ABS.
8. DBHBT is a poor photo - stabilizer for ABS.,
9. The photo - degradation of ABS is a first - order process proceeding through double bond oxidation. The rate constant for the double band destruction is 8.668×10^{-6} sec^{-1}.

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10. Hydroxyl groups appear to be oxidation products of the double bond oxidation and these hydroxyl groups are converted to carbonyl groups

11. Formation of carbonyl groups lead to yellow colouration of the polymer.

12. It appears that the increasing build-up of carbonyl groups corresponds to the increasing intensity of the yellow colouration with time of ageing.

5.5 Thermal Oxidation of ABS

Fig. 8 shows the spectra of thermally degraded ABS. Hydroxyl/ and carbonyl bands can be seen to grow at 3500cm^{-1} and 1725cm^{-1} respectively. At the initial stage of heating, bands are observed to grow at 1650 and 1820cm^{-1} in addition to the carbonyl group centered at 1725cm^{-1}. These species are probably unsaturated acid (1650cm^{-1}) and ketone (1825cm^{-1}). Scott[1] also reported similar observations at 1665, 1685 and 1699cm^{-1}. From the spectra, it could be observed that these species accumulate more slowly than saturated carbonyl (1725cm^{-1}) and during further heating, they became shoulders of the dominating saturated carbonyl band.

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It can be seen that the - C = C - stretching bond of the terminal double bond at 1507cm^{-1} increases slightly after some time. This may suggest that undersevere and long heating, some scission of the polymer chain do occur. Polytrans - 1, 4 - butadiene and polycis - 1, 2-butadiene bands at 965 and 910cm^{-1} respectively diminish with time. The degraded samples have been found to develop intense yellow colouration and finally becoming insoluble in dichloromethane.

5.6 Effect of processing time on stabilizer activity

The effect of thermal processing on the efficiency of DBHBT is represented in Fig. 9. Samples 1 - 4 all contain DBHBT physically mixed and thermally processed for 2, 3, 5 and 7½ minutes repectively in ascending order. Sample 5 contains DBHBT grafted into the polymer matrix and processed for 7½ minutes.

The values of induction periods and embrittlement times have been presented in table IX. It is clear from Fig. 9 that the bound stabilizer is much more efficient than physically mixed stabilizers. The sample containing grafted DBHBT has a carbonyl induction time of 494hrs and embrittlement time of 2250hrs while the other sample which contain physically mixed DBHBT and processed for an equal time of 7½ mins.

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has a carbonyl induction time of 296hrs and embrittlement time of 505hrs. It is also evident from the samples containing DBHBF which have been physically mixed with the polymer that 3 minutes appear to be the most economical processing time.

The poorer stability imparted to samples processed for 5 and $7\frac{1}{2}$ mins. is believed to be due to excessive heating which is capable of introducing some hydroperoxides into the sample. Since hydroperoxides are quite photosensitive, the net effect is that the stabilizer level are somewhat lowered by the consumption of the hydroperoxides produced during heat treatment. On the other hand, after only 2 mins. of processing, it is probable that the stabilizer has not been evenly mixed with the base polymer. This may not only lead to agglomeration of the stabilizer, in which case it is, in effect, underemployed., but may also lead to loss by volatilization during processing. The lower initial carbonyl content of the sample processed for 2 mins may suggest that the least thermo-oxidative degradation occured during processing.

The unstabilized sample (control) degrades without any period of induction and embrittles after only 12hrs. In sample 1, the induction period to the on set of destruction of the - C = C - bonds is increased

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from 0 (unstabilized) to 168hrs, while in sample 4, it has been increased further to 292hrs. Of the physically mixed samples, the sample processed for 3mins. exhibits the longest induction period of 350hrs while sample 3 shows an induction period of 305hrs. The sample processed for 3 mins. also has the highest embrittlement times as can be seen in table. II. These performances indicate that DBHBT is a powerful thermal stabilizer.

That the grafted stabilizer is much more superior to the physically mixed ones is vividly borne out in Fig. 9 (5) and from both the induction periods and embrittlement times shown in table II. Kolawole[2] has observed similar behaviour with BHBM and EBHPT added as bound masterbatches to ABS. (BBHBT used in this present work is an ester of BHBM.) Tahan[3] also demonstrated that grafting, by copolymerizing HOBT with ABS significantly improved the induction period and consequently the embrittlement properties and decreased the rate of oxidation. Technologically, this is of immense importance. The following advantages are at least immediately feasible. By being grafted, the stabilizer becomes non-volatile and ensures maximum utilization. Lower level of incorporation will be required unlike the conventional, physically mixed stabilizers where high

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concentrations are necessary since the stabilizers are uniformly dispersed in the whole matrix of the polyblend although the major degradation occurs in the rubber moiety. Added to the advantage of being effective at much lower concentrations is the fact that bound stabilizers are completely resistant to solvent extraction and leaching processes. Grafting also reduces the problem of incompatibility which would have greatly reduced the efficiency of the stabilizers.

5.7 First - order plots.

Fig. 10 shows the linear plots of the growing concentrations of carbonyl and hydroxyl groups and the diminishing concentration of the polytrans - 1, 4 - butadiene at 965cm^{-1}. The curves show short periods of induction. The straight lines obtained after the initial periods show that thermal - oxidative degradation of ABS also follows a first order process as has been found in photo-oxidative degradation.

The rate of loss of unsaturation in the rubber segment can be seen from this plot to be quite similar to the rate of formation of hydroxyl groups. Calculated values of rate constants for - C = C - and - O - H are 12.337 and 11.810 x 10^{-6} sec^{-1} respectively. This is indicative of the dependence of hydroxyl formation on double bond destruction. It may be concluded that thermal oxidation of ABS is a first

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order process and proceeds through double bond destructive oxidation. In all the cases studied, carbonyl groups appear only after some hydroxyl groups have been formed. This observation suggests that carbonyl formation is a secondary process probably as a result of conversion of hydroxyl groups.

In the presence of 1.0%DBHBT, the initiation process for the degradation of the polymer i.e. the destruction of the double bonds is greatly suppressed. The unstabilized sample has no significant period of induction while that of 1.0%DBHBT processed for the same length of time of 3 mins. exhibits an induction period of 350hrs. Also, the time to embrittlement of 680hrs obtained with the stabilized sample is much more superior to the unstabilized sample of 24hrs. as shown in table II. In essence, the useful life of the product has been extended by about 30times.

5.8 Phenyl and Nitrile groups

Fig. 11 shows the changes occuring in phenyl (11a) and nitrile (11b) groups. Essentially, there is no significant change in the acrylonitrile group as can be observed from the ir spectra of fig. 8.

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On the other hand, under prolonged heating, some chemical modifications seem to occur with the phenyl group. The process involved may be more complex but it is thought to be associated with the changes observable at 1587cm^{-1}. The increase in absorption at 1587cm^{-1} which is due to the stretching of - C = C - bond is believed to be due to chain scission which increases the concentration of the terminal carbon - carbon double bonds. It is probable that these double bonds are adjacent to the phenyl group, and as such, affect the behaviour of the phenyl group at 1960cm^{-1} (see fig. 8). In making this proposal, it is thought that the observed terminal double bond unsaturation occurs in the polystyrene component of ABS, resulting in a structure given below.



5.9 Hydroperoxide - decomposing activity of DBHBT

The dependence of hydroxyl index on heating time is shown in fig. 12 for samples containing 1.0% DBHBT and processed for different times. The shapes of all the curves are similar.

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A general fall in the hydroxyl index is observed for all the samples. (This situation has been found in all samples containing DBHBT which have been thermally degraded). After this initial fall, the hydroxyl group concentration remains constant for sometime after which it then grows. This behaviour may be rationalized as follows. Hydroxyl groups which were produced in the polymer during the thermal processing are converted to peroxides which are consumed by the sulphide group of the stabilizer. This also explains the constancy of the carbonyl peak at 1725cm^{-1} during this period as stated earlier. However, when the level of the sulphide has fallen substantially, the hydroxyls produced are gradually converted to carbonyls which is then reflected in the growing peak at 1725cm^{-1}.

This observation suggests that DBHBT acts as a peroxide decomposer. This result is similar to that obtained by Kolawole[2] who discovered that the initial hydroxyl group in ABS decreased in the presence of BHBM as stabilizer.

5.10 Comparison of DBHBT and Tinuvin P as thermal Stabilizers.

The stabilizing effectiveness of DBHBT and Tinuvin P during thermal - oxidative degradation can be compared from fig. 13.

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This figure represents the destruction of polytrans - 1, 4 - butadiene at 965cm^{-1} with heating time.

In agreement with other results obtained in this work the unstabilized sample is the least stable and consequently degrades fastest. This sample degrades without exhibiting any appreciable time of induction. Tinuvin P is a very poor thermal stabilizer as it only gives an induction time of about 50hrs. In fact, technologically, it should not be regarded as a thermal stabilizer. On the contrary, DBHBT is a powerful thermal stabilizer. At 1% level added conventionally, the time to embrittlement has been increased by over 600hrs. A greater improvement has even been achieved when DBHBT is grafted to the polymer as the embrittlement time has been increased by over 2000hrs. (see table II).

The difference in the initial concentration of unsaturation content is attributable to the thermal history of the samples. The unstabilized sample has the lowest initial content of double bonds. This means that the greatest damage was done to this sample during the thermal processing. The least damage was done to the sample containing DBHBT because as as good thermal stabilizer, it offered the greatest protection to ABS.

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In this way, the polybutadiene segment was retained. The lower level found in Tinuvin P - stabilized sample confirms that Tinuvin P is a poor thermal stabilizer. Otherwise, it should have effectively protected ABS during the 3 mins. of processing as can be said in the case of DBHBT.

5.11 Effect of Extraction

Films containing Tinuvin P and DBHBT were extracted with hot cycylohexane for 48hrs. and the stability of the samples to heat was then studied. Fig. 14 shows the changes observed in the carbonyl index.

The unstabilized sample shows no defference between the extracted and unextracted samples in the rate of degradation. On the other hand, extracted films containing Tinuvin P degrade faster and embrittle earlier than the unextracted films. The times to embrittlement for the extracted and unextracted samples are 122 and 154hrs. respectively. It is clear from fig. 14 that the extracted samples as still more stable than the unstabilized sample. This may probably suggest that not all of the stabilizer present in the polymer has been fully extracted or could be extracted.

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It can be seen that the extracted film containing DBHBT still exhibits substantial time of induction. This tends to indicate that 40hrs. of hot extraction in cyclohexane has not totally removed the stabilizer from the polymer matrix. It has been observed that the grafted sample is completely indifferent to extraction as no noticeable change occured. This tends to confirm that bound stabilizer systems are completely resistant to solvent extraction and leaching. Similar results have been obtained by some other workers. Tahan[3] found that 2, 4-dihydroxybenzophenone, a UV absorber and some of its derivatives are more efficient when grafted to the polymer matrix and also resistant to solvent extraction. It has also been shown by Scott[4] that antioxidants can be effectively bound unto rubber to give solvent and detergent resistant vulcanisates. Similar studies[5] in ABS have indicated that a 2-hydroxybenzophenone (BHPA) containing a polymerizable vinyl group can be copolymerized with styrene and acrylonitrile to give modified ABS containing the parent dihydroxybenzophenone but with improved resistance to solvents.

The importance of the result obtained in this present work is that grafting of the stabilizer, among other things, ensures permanence,

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which is one of the important technological criteria of choosing stabilizers for polymer products. And, when such products are used in preserving foodstuffs, liquids and solutions, the problem of contamination arising from the dissolution of the stabilizer is completely eliminated. The relevance of this as regards health hazards may not be overestimated. Grafting also helps in preventing volatilization of the stabilizers. This helps to maintain the concentration level of the stabilizer as well as reducing atmospheric pollution.

5.12 Natural weathering

Results of ABS films exposed to natural atmospheric conditions are presented in figs 15-18 and in table III.

Fig 15 shows the changes of the functional groups during natural weathering of ABS. The loss of unsaturation occurs rapidly without any period of induction. The growth of hydroxyl groups has an induction period of 2hrs while the carbonyl group grows after an initial induction period of 4hrs. It is clearly seen that the growth of the hydroxyl group levels up when the unsaturated content of polybutadiene has been completely destroyed. This observation is consistent with the findings during thermal and photo - degradation studies reported earlier, and

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shows that - OH and >C = O are produced after the - C = C - bond has been attacked and its breakdown started. Thus showing that oxidation proceeds with the attack on the double bonds. The carbonyl group continues to grow during the period of exposure, even after the hydroxyl group has reached its peak. This further growth of the carbonyl group is at the expense of the hydroxyl group which is seen to diminish with the growth of the carbonyl. It may thus be concluded that hydroxyl groups are only intermediates in the oxidative reactions of degradation and ultimately become converted to saturated carbonyl groups.

The yellow colouration observed in degraded samples of ABS and which grows in intensity with the time of exposure may thus be probably due to the production of carbonyl groups.

The dependence of the carbonyl index on exposure time is presented in Fig. 16. The unprotected sample suffers the greatest damage under natural weathering. A sharp increase in the carbonyl index of this sample occurs and embrittles after only 6hrs. of exposure. The increases in the stabilized samples are slower and occur after initial induction periods. It appears that the two stabilizers, Tinuvin P and DBNBP exhibit some stabilizing effects after the induction periods,

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This pre - induction behaviour may probably be a result of inhibition of the degradative processes by the breakdown products of the stabilisers.

Fig. 17 shows the changes occuring in polytrans - 1, 4-butadiene content of ABS during natural weathering. The stability confered upon the polymer by the stabilizers appear in form of prevention of the destruction of the polybutadiene unsaturation during the induction period. The shapes of these curves are similar to the corresponding ones obtained during thermal and photo - degradation. This suggests that degradations under these conditions is similar. The longer induction period of the sample containing Tinuvin P shows that this stabilizer performs better than DBHBT under natural weathering conditions.

Fig. 18 shows the first - order plots of the dependence of polytrans - 1, 4-butadiene unsaturation on exposure time under various conditions in which the samples have been exposed. The rate constants obtained are as shown below.

Additive	K values (in 10^{-6} sec^{-1})		
	UV	Oven	Natural Weathering
None	9.383	10.395	13.328
DBHBT	-	-	6.752
Tinuvin P	-	-	10.236

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The rate constants indicate that the unstabilized sample degraded fastest under natural atmospheric conditions and least under artificial ultraviolet irradiation. This observation is not easily comparable. One of the reasons for lack of adequate correlation between accelerated indoor and atmospheric tests may be the presence of ozone in different concentrations under the test conditions. Also, some components of the atmosphere are markedly photosensitive and could well lead to oxidative reactions of the polymer under natural conditions which will be absent under artificial conditions. The effects of moisture and other adventitious impurities may also be contributory.

Under oven ageing, the films are subjected to more or less a constant source of heat energy since the air oven is thermostated at 100 + 1°C. Similarly, films were irradiated with a UV lamp of 254mm wavelength. It may be appreciated therefore that the times of exposure for thermally degraded and UV irradiated films are approximate measures of total energy absorbed. On the other hand, because of daily variations in weathering conditions, the time scale for natural weathering is merely an arbitrary measure of expesure. Also, night and day conditions imposed on the films can create some stress which may affect the degradation of these samples.

..../70.

These are some of the inherent limitations in comparing the observed results.

Despite the difficulties enumerated above, one may still rationalize the observed behavior. Under atmospheric conditions, it is expected that degradation of polymers results from the combined effects of oxygen, ozone, heat, moisture, ultraviolet radiation and perhaps, microorganisms. Obviously, the combined effects will be to accelerate the rate of degradation over what may be anticipated under the individual effects of heat or UV irradiation alone.

It is of interest that straight lines are obtained in all these plots (fig. 18) after the initial induction period. This means that degradation follows first - order kinetics for the disappearance of polytrans 1, 4-butadiene unsaturation. It may be concluded that the mechanisms of degradation are essentially the same under natural weathering oven ageing and UV irradiation.

5.13 Summary of observations and suggestions.

The following observations have been made from the results of this work.

During the ageing of the polymer films, the polybutadiene content

..../71.

decreased and oxidative products containing hydroxyl and carbonyl groups were produced. It appears that the hydroxyl products are intermediates probably in the form of hydroperoxides and are responsible for the formation at least initially of the carbonyl groups. These carbonyl groups are believed to be responsible for the yellow colouration observed in degraded samples of ABS. The increasing growth of the carbonyl groups with exposure time is believed to correspond to the growing intensity of colouration as degradation reactions proceeded.

The oxidative reaction is thought to occur in two parts. The initiation process, involving mainly the formation of hydroperoxides induced by radical production; then a second subsequent process, initiated by the decomposition of the hydroperoxides which induces chain reactions. In order to explain the results of the infrared spectra, the following general scheme is proposed:

Initiation: RH (polymer) $\longrightarrow$ free radicals (1)

$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$ ... ... (2)

$RO_2^{\bullet} + RH$ (or AH) $\longrightarrow$ ROOH + $R^{\bullet}$ (or $A^{\bullet}$) ... (3)

$RO_2^{\bullet} + R^{\bullet}$ (or $RO_2^{\bullet}$) $\longrightarrow$ ROOR (+ O_2) ... (4)

ROOR, ROOH $\longrightarrow$ R - OH + R = O ... (5)

..../72.

$$ROOH \longrightarrow RO_2^{\bullet} + {}^{\bullet}H; \quad RO^{\bullet} + {}^{\bullet}OH \quad \ldots \quad (6)$$

$$RO^{\bullet} + RH \text{ (or AH)} \longrightarrow ROH + R^{\bullet} \text{ (or } A^{\bullet}) \quad \ldots \quad (7)$$

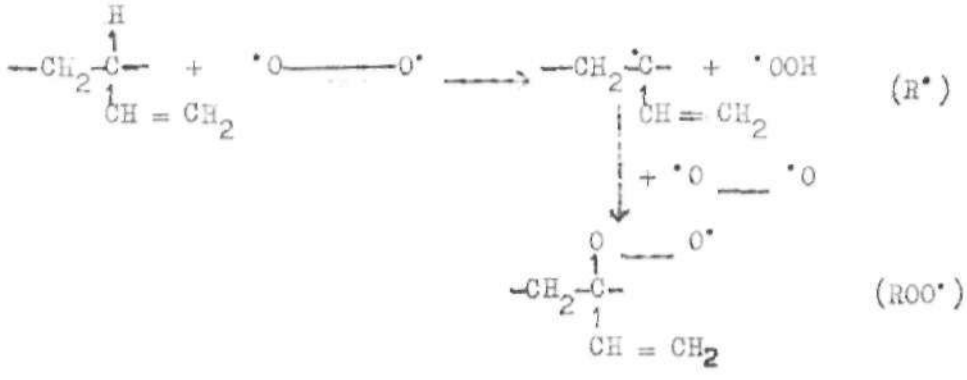
$$R \text{ ..... } RO^{\bullet} \longrightarrow R^{\bullet} + R = O \quad \ldots \quad (8)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \quad \ldots \quad \ldots \quad (9)$$

$$RO_2^{\bullet} + RH \text{ (or AH)} \longrightarrow ROOH + R^{\bullet} \text{ (or } A^{\bullet}) \quad \ldots \quad (10)$$

$$ROOH \longrightarrow \text{Non - volatile products } (-OH, \quad CO) \quad (11)$$

The degradation of polymer is generally initiated by the formation of polymeric (free) radicals. In the degradation of the polymer, hydrogen abstraction by oxygen or photolytic ejection of a proton is considered to predominate in the initiation process. As the ABS resin contains some double bonds, the C - H bond in the - carbon position would be especially labile to oxidize.



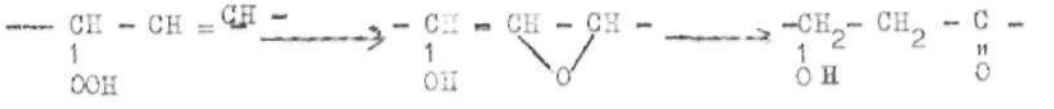
These radicals ($R^{\bullet}$ and $RO_2^{\bullet}$) are very reactive and they react easily as shown in reactions (2) - (4) above. In this stage of oxidative degradation of polymers, the effect of the presence of a stabilizer becomes quite obvious (reaction (3).

..../73.

A good stabilizer consumes the alkylperoxy radicals such that the polymer is protected at the sacrificing expense of the antioxidant, AH.

Due to the high reactivity of the radicals $RO_2^{\bullet}$ with labile hydrogen (e.g. hydrogen attached to the α- methylene of the double bond or tertiary hydrogen) hydroperoxides gradually accumulate. Reactions leading to the production and accumulation of hydroperoxides thus constitute the first part of the oxidative degradation of the resin.

The second stage reactions then begin with hydroperoxide decomposition reaction (6) which induces the auto-oxidative reactions. The radical RO' acts as a chain carrier as depicted by reactions (7) and (8) while hydroxyl and carbonyl groups are produced. The chainscission reaction may effectively occur at the 1, 4-polybutadiene structure which, according to Szwarc[6], has the weakest carbon - carbon bond energy (38 Kcal/mol) in this polymer. If the hydroperoxide group is produced at the α - carbon position of the double bond, ozonide structure may probably be produced as below.



..../74.

While the above has been proposed for the general degradation of ABS resin, it must be pointed out that the initiation of the polymer to yield polymeric radicals may be slightly different under the conditions studied in this work. Under oven ageing, initiation may purely be due to thermal energy; while protons may be photolytically ejected during UV irradiation. Under natural atmospheric conditions, hydrogen may be abstracted by the diradical nature of oxygen i.e.

$$R - H \xrightarrow{hv,\ heat} R^{\cdot} + H^{\cdot}$$

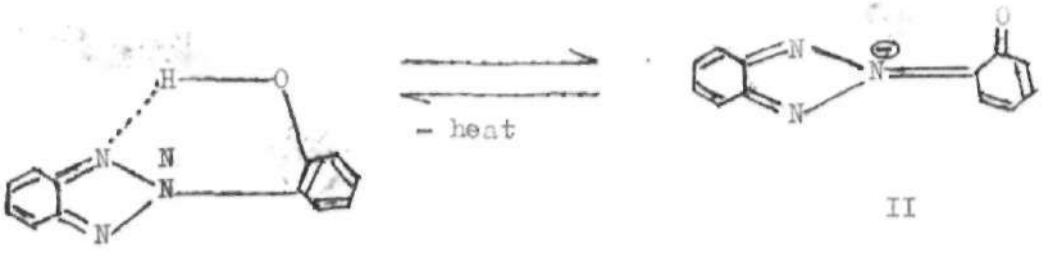
or $^{\cdot}O __ O^{\cdot}$

Reaction (10) also indicates the role of stabilizers in the second stage of oxidative degradation reactions. Stabilizers can scavenge alkylperoxides and other free radicals, thus preventing their attack on the polymer backbone. The autocatalytic effect of hydroperoxides can clearly be seen from reaction (6) since free radicals are produced which accelerate the oxidative reactions of ABS resins. Consequently, peroxide decomposing stabilizer DBHBT imparts considerable stability to ABS.

Tinuvin P possesses an intramolecular hydrogen-bonding and a structure formally related to the 2-hydroxybenzophenones.

..../75.

Therefore, a phototautomerism may also occur with Tinuvin P. The existence of such a "photoenol" such as below is purely suggestive.



I II

It is thus thought that I is rapidly converted to a "photoenol" (II) by absorption of light and that II reverts to I with loss of energy as heat, with a very high efficiency comensurate with the good UV stabilizing activity of Tinuvin P (I).

..../76.

C O N C L U S I O N S

It has been found that unstabilized PS, PMMA and ABS degrade readily under oven ageing, UV irradiation and natural atmospheric weathering and that the stability of these polymers has been improved by the incorporation of stabilizers.

The relative stabilizing effectiveness, under UV irradiation of the stabilizers employed is in the order ZnDEC DBHBT Irganox 1976. On the other hand, as thermal stabilizers, the increasing order of effectiveness is Irganox 1076 ZnDEC DBHBT. Since Irganox 1076 is used commercially as a thermal stabilizer, the use of DBHBT as a substitute is highly recommended.

A two component stabilizer of ZnDEC and DBHBT performs much better thermally and should be preferred to Irganox 1076 or DBHBT alone. Also, the two component mixtures of Irganox 1076/ZnDEC, Irganox 1076/DBHBT and ZnDEC/DBHBT have all been found to show synergism.

The degradation of ABS has been found to start with the attack of the polybutadiene content and that oxidation products containing hydroxyl and carbonyl groups are produced. DBHBT has been found to be a powerful thermal stabilizer but a rather poor UV stabilizer for ABS.

..../77.

On the other hand, Tinuvin P is a poor thermal stabilizer but a good UV stabilizer. The grafted stabilizer (DBHBT) performs much more efficiently than the one which was physically mixed. Grafting of stabilizers is therefore a better way of protecting polymers against degradation than mere physical mixing with the polymer.

Suggestions for further work

It would be desirable, to monitor the volatile products during the degradation of PS, PMMA and ABS when such equipments are available in the Department. This would help immensely in understanding the mechanism of degradation and thus help in designing effective ways of stabilizing the polymers. It is also helpful to measure the amount of oxygen absorbed as degradation proceeds.

Three - component mixtures of the stabilizers should be investigated. Perhaps, a greater synergism may be obtainable at a lower stabilizer concentration. Attempts should also be made in preparing a single compound which might be able to act simultaneously as a thermal and UV stabilizer (i.e. a homosynergist).

..../78.

Table I: I.P. and E.T for UV irradiation

Material	Processing time (mins.)	Time to embrittlement (hrs.)	Induction Period			
			-C=C- $965cm^{-1}$	-O-H $3450cm^{-1}$	C=O $1725cm^{-1}$	-C=C- $910cm^{-1}$
Unstabilized ABS/pressed	3	68	0	2	4	0
ABS/1% DBHBT/pressed	2	2500	15	16	18	15
"	3	2500	35	38	42	35
"	5	2500	22	26	29	22
"	7½	2500	18	22	25	18
ABS/1% DBHBT/grafted/ pressed ...	7½	2500	74	78	80	74
Unstabilized ABS/cast	3	65	0	2	4	0
ABS/1% DBHBT/cast	2	2500	15	16	18	15
"	3	2500	35	38	42	35
"	5	2500	22	26	29	22
"	7½	2500	18	22	25	18
ABS/1% DBHBT/grafted/ cast ...	7½	2500	44	48	50	44
ABS/0.25% T.P./pressed	3	2500	115	118	120	115
"	3	2500	305	307	308	305
ABS/1.0% T.P./pressed	3	2500	814	815	816	814
ABS/2.0% T.P./pressed	3	2500	813	815	816	813
ABS/0.25% T.P./cast	3	2500	115	118	120	115
ABS/0.50% T.P./cast	3	2500	304	306	308	304
ABS/1.0% T.P./cast	3	2500	814	815	816	814
ABS/2.0% T.P./cast	3	2500	812	814	815	812

..../

Table II: I.P. and E.T. for Oven ageing.

Material	Processing Time (hrs.)	Time to embrittlement (hrs.)	Induction Period			
			-C=C- 965cm^{-1}	-O-H 3450cm^{-1}	C=O 1725cm^{-1}	-C=C- 910cm^{-1}
Unstabilized ABS/pressed	3	24	0	2	2	0
ABS/1% DBHBT/pressed	2	470	168	172	174	168
"	3	680	350	354	354	350
"	5	620	305	308	310	305
"	7½	585	292	294	296	292
ABS/1% DHBHT/grafted/ pressed ...	7½	2250	480	483	484	480
Unstabilized ABS/cast	3	12	0	2	2	0
ABS/1% DBHBT/cast	2	400	166	170	171	166
"	3	632	350	354	354	350
"	5	578	303	305	306	303
"	7½	528	290	292	294	292
ABS/1% DBHBT/grafted/ cast ...	7½	2120	476	480	482	476
ABS/0.25% T.P./pressed	3	35	8	10	12	8
ABS/0.50% T.P./pressed	3	52	13	15	16	13
ABS/1.0% T.P./pressed	3	68	22	24	26	22
ABS/2.0% T.P./pressed	3	68	22	24	26	22
ABS/0.25% T.P./cast	3	32	8	10	12	8
ABS/0.50% T.P./cast	3	48	13	15	16	13
ABS/1.0% T.P./cast	3	58	21	23	25	21
ABS/2.0% T.P./cast	3	58	20	23	24	20

..../

Table III: I.P and E.T. under natural weathering.

Material	processing time (.irs)	time to embrittlement (hr)	Induction Period			
			-C=C- 965cm^{-1}	-O-H 3450cm^{-1}	C=O 1725cm^{-1}	-C=C- 910cm^{-1}
Unstabilized ABS/cast	3	8	0	2	3	0
ABS/1% DBHBP/cast	2	120	88	90	92	88
"	3	285	148	150	152	126
"	5	152	134	135	136	134
"	7½	138	132	134	137	132
ABS/1% DBHBP/grafted/ cast ...	7½	1500	226	228	230	226
ABS/0.25% Tin./cast	3	310	122	124	126	122
ABS/0.50% Tin. /cast	3	454	142	158	60	156
ABS/1.0% Tin./cast	3	1460	156	194	196	192
ABS/2.0% Tin./cast.	3	1472	194	195	197	194

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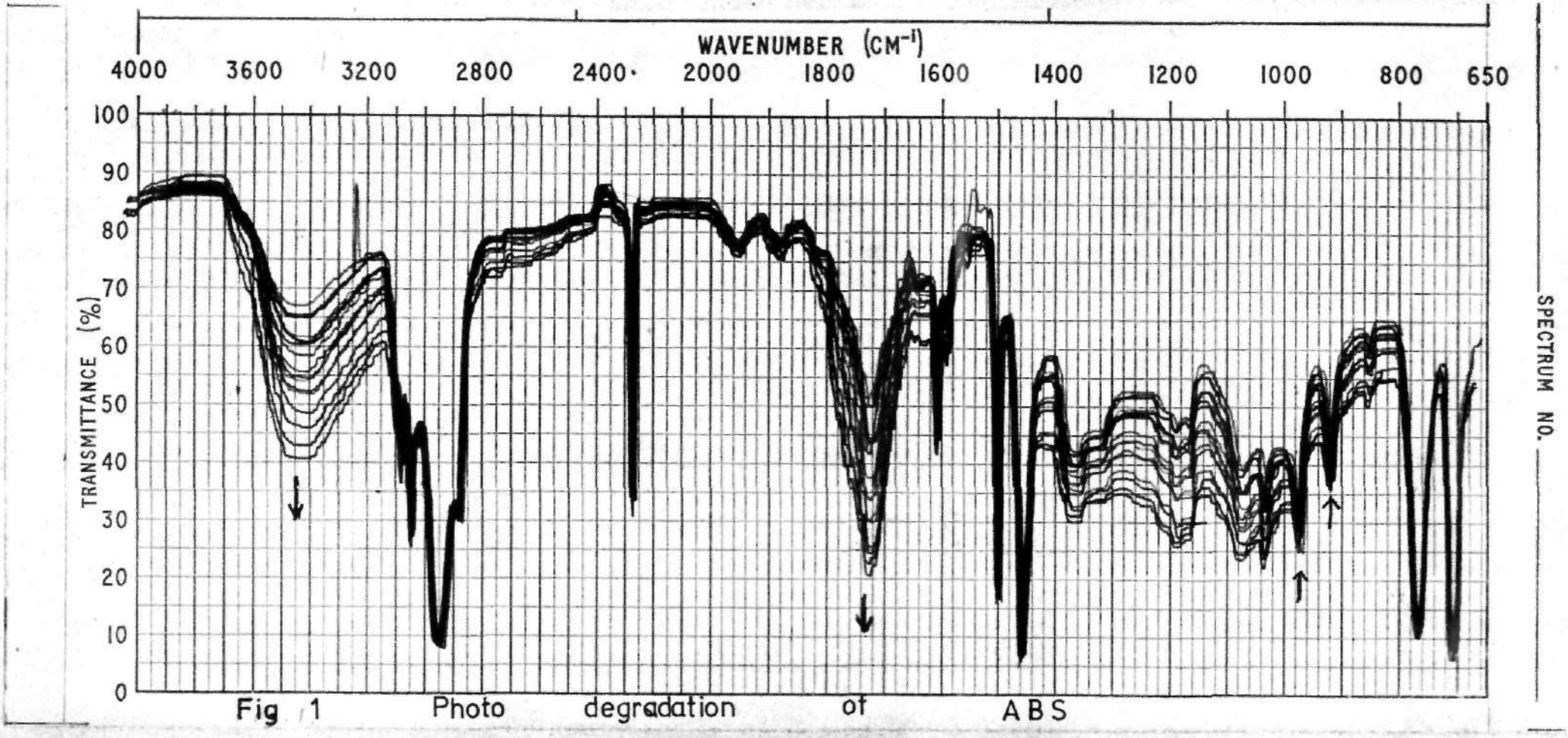
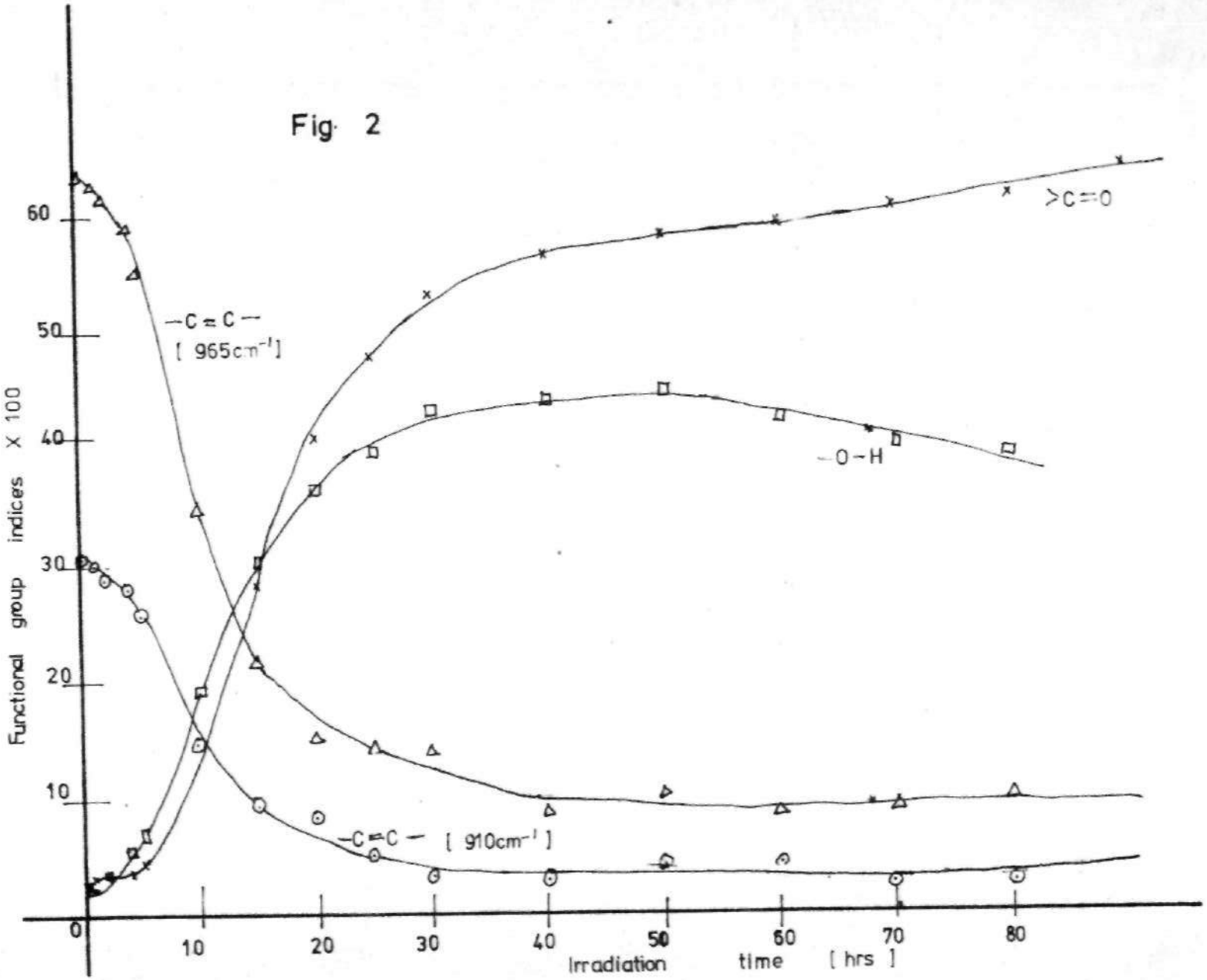


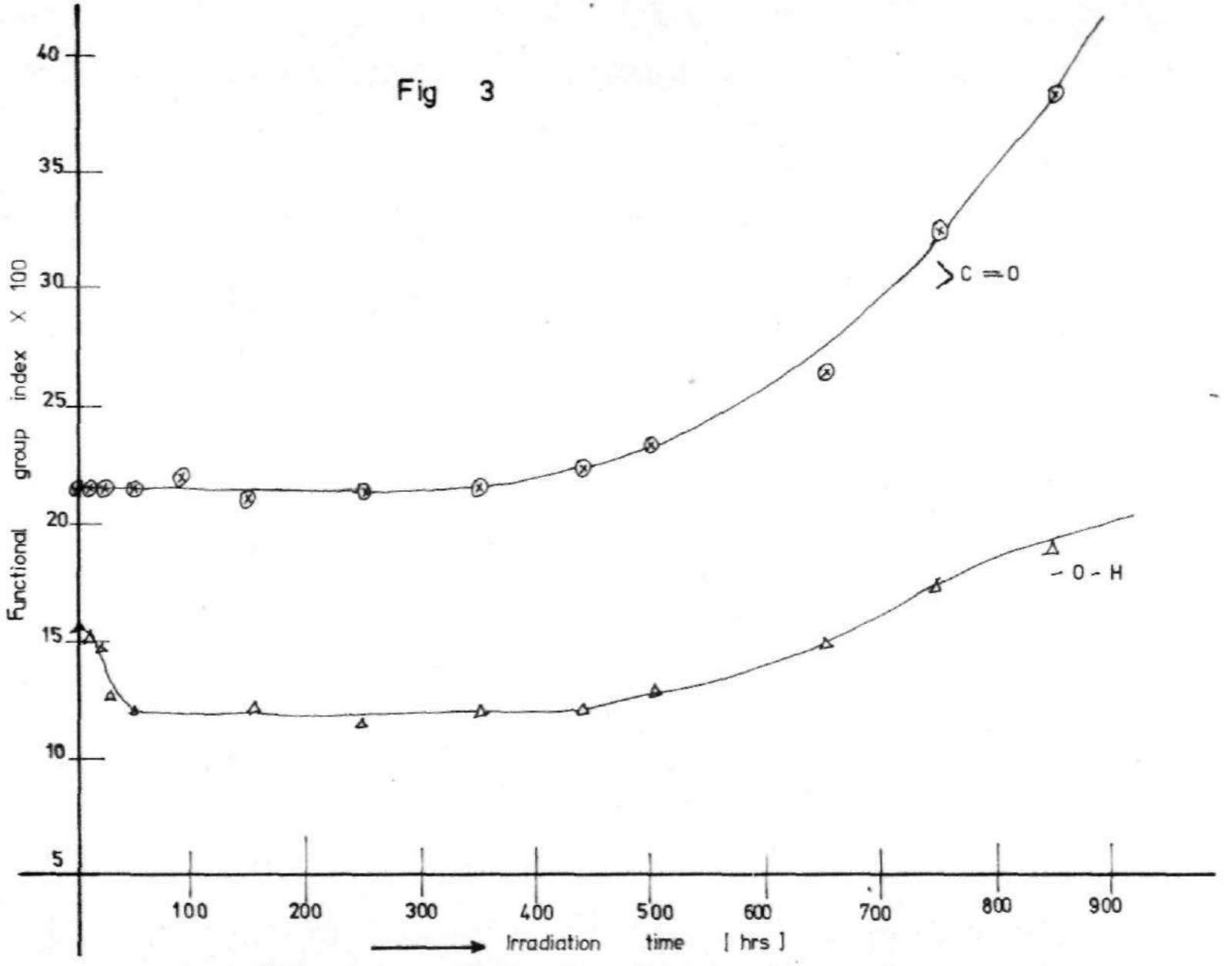
Fig 1 Photo degradation of ABS

Fig. 2



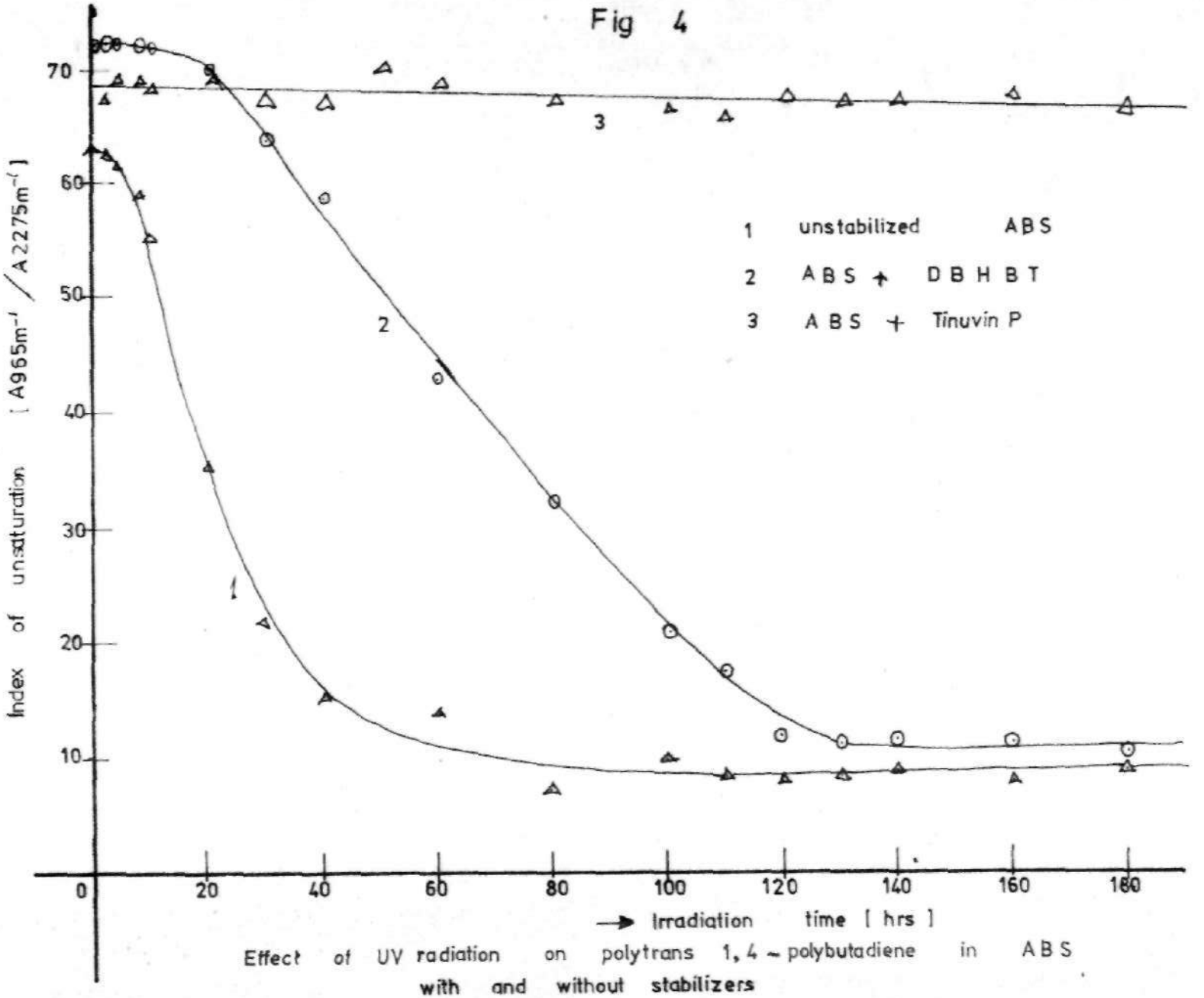
Effect of UV radiation on functional group indices in unstabilized ABS

Fig 3



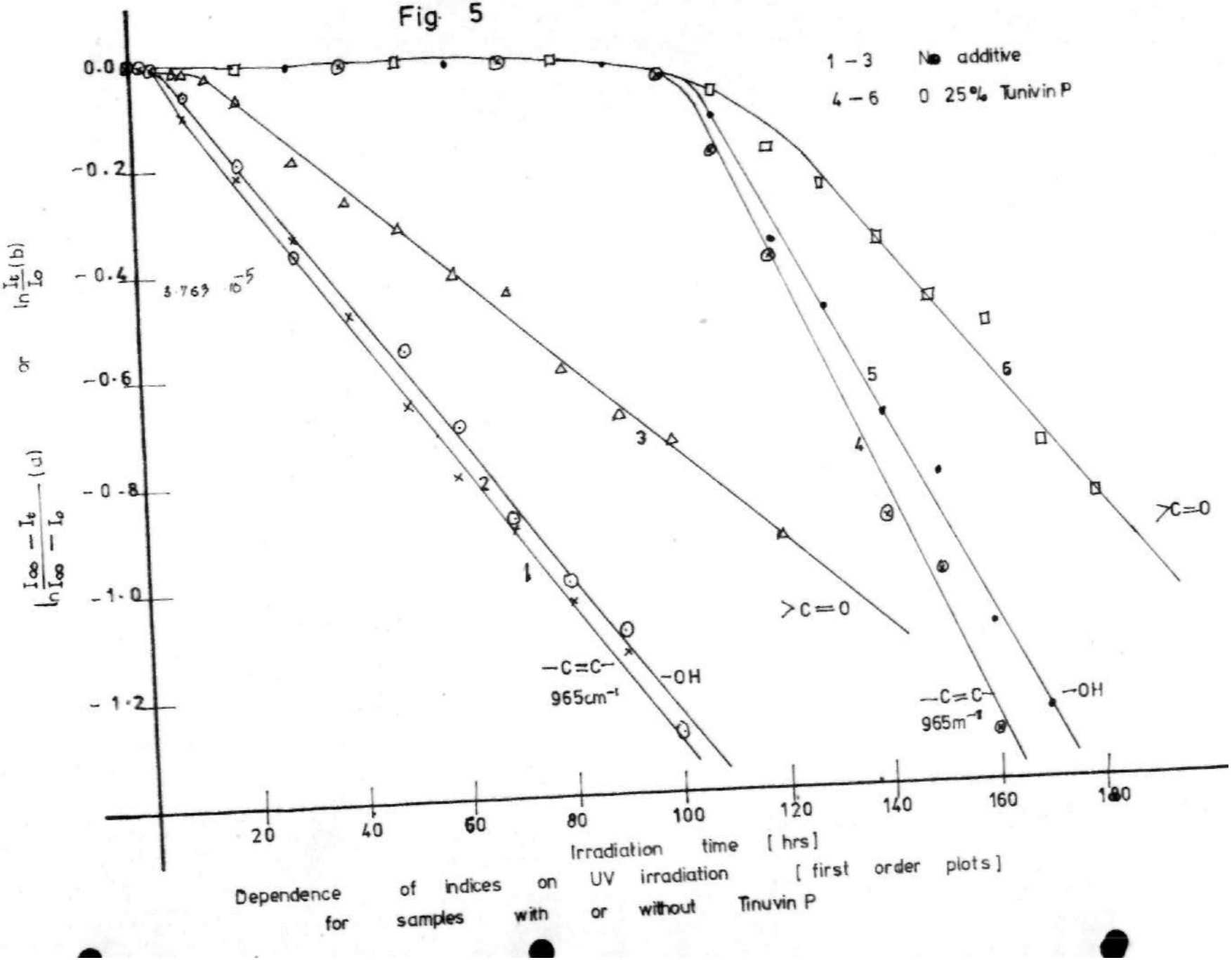
Changes in carbonyl and hydroxyl indices of a sample containing DBHBT

Fig 4



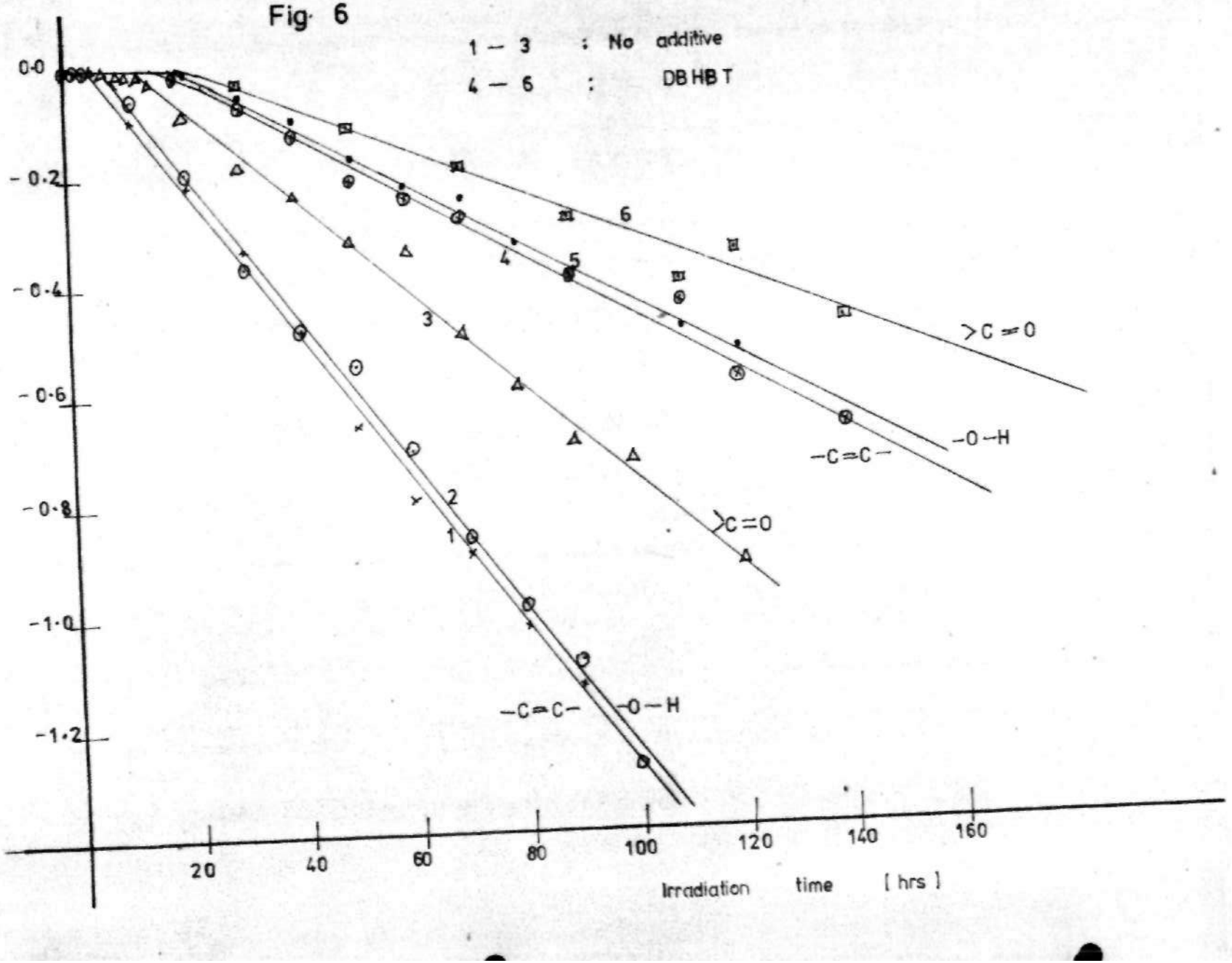
Effect of UV radiation on polytrans 1, 4 – polybutadiene in ABS with and without stabilizers

Fig 5

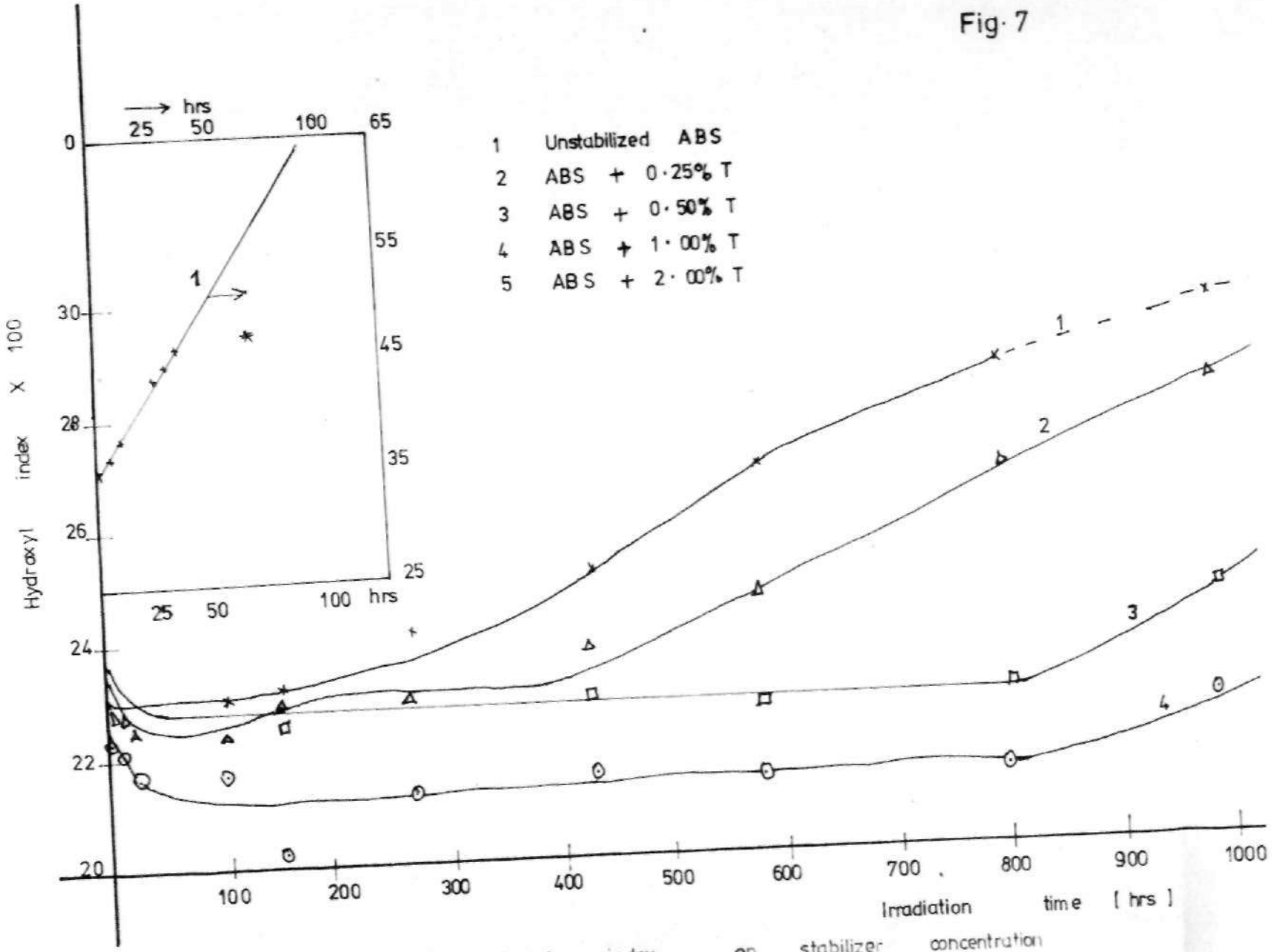


Dependence of indices on UV irradiation [first order plots]
for samples with or without Tinuvin P

Fig. 6


1 — 3 : No additive
4 — 6 : DBHBT
0·0
- 0·2
- 0·4
- 0·6
- 0·8
- 1·0
- 1·2
20
40
60
80
100
120
140
160
Irradiation time [hrs]
>C=O
-O-H
-C=C-
>C=O
-C=C-
-O-H

Fig· 7



Dependence of hydroxyl index on stabilizer concentration under UV irradiation

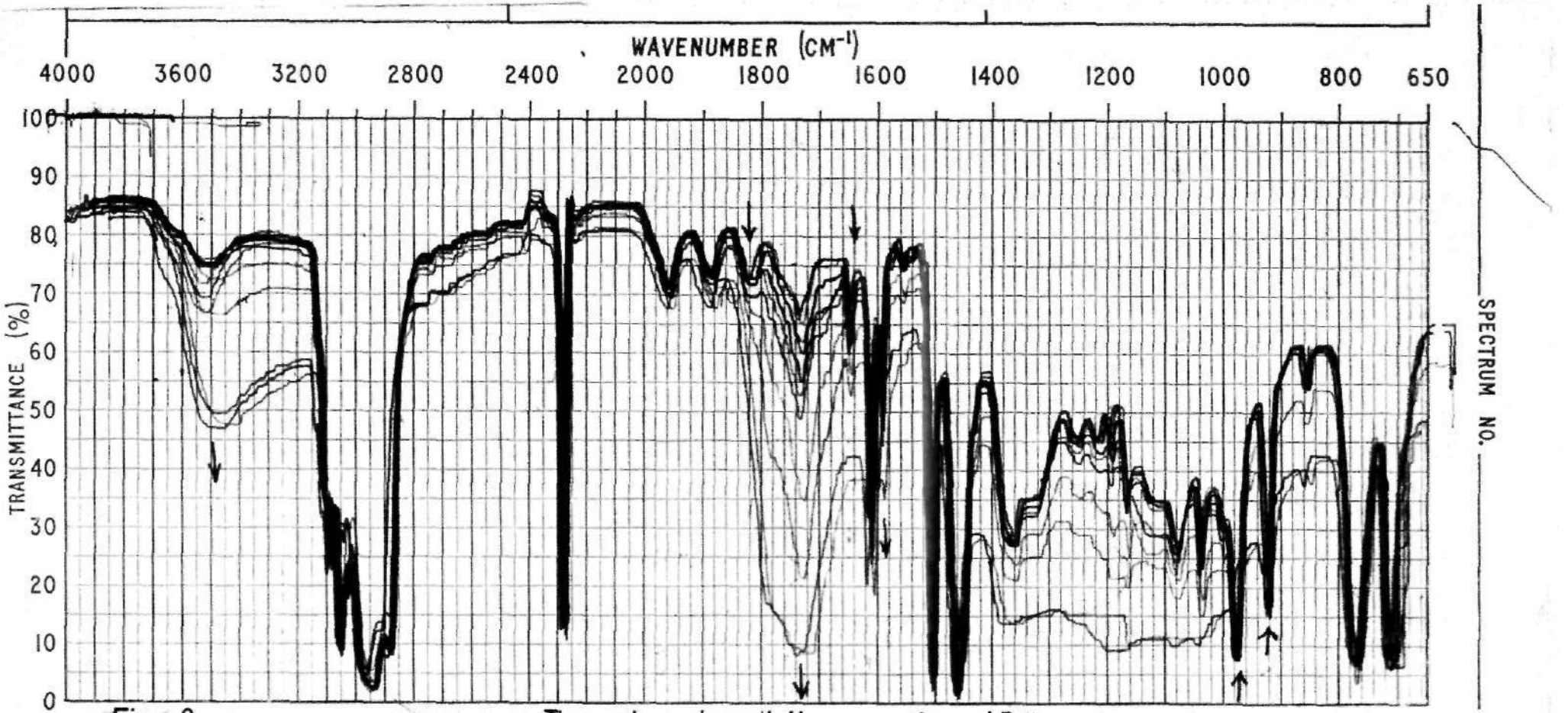
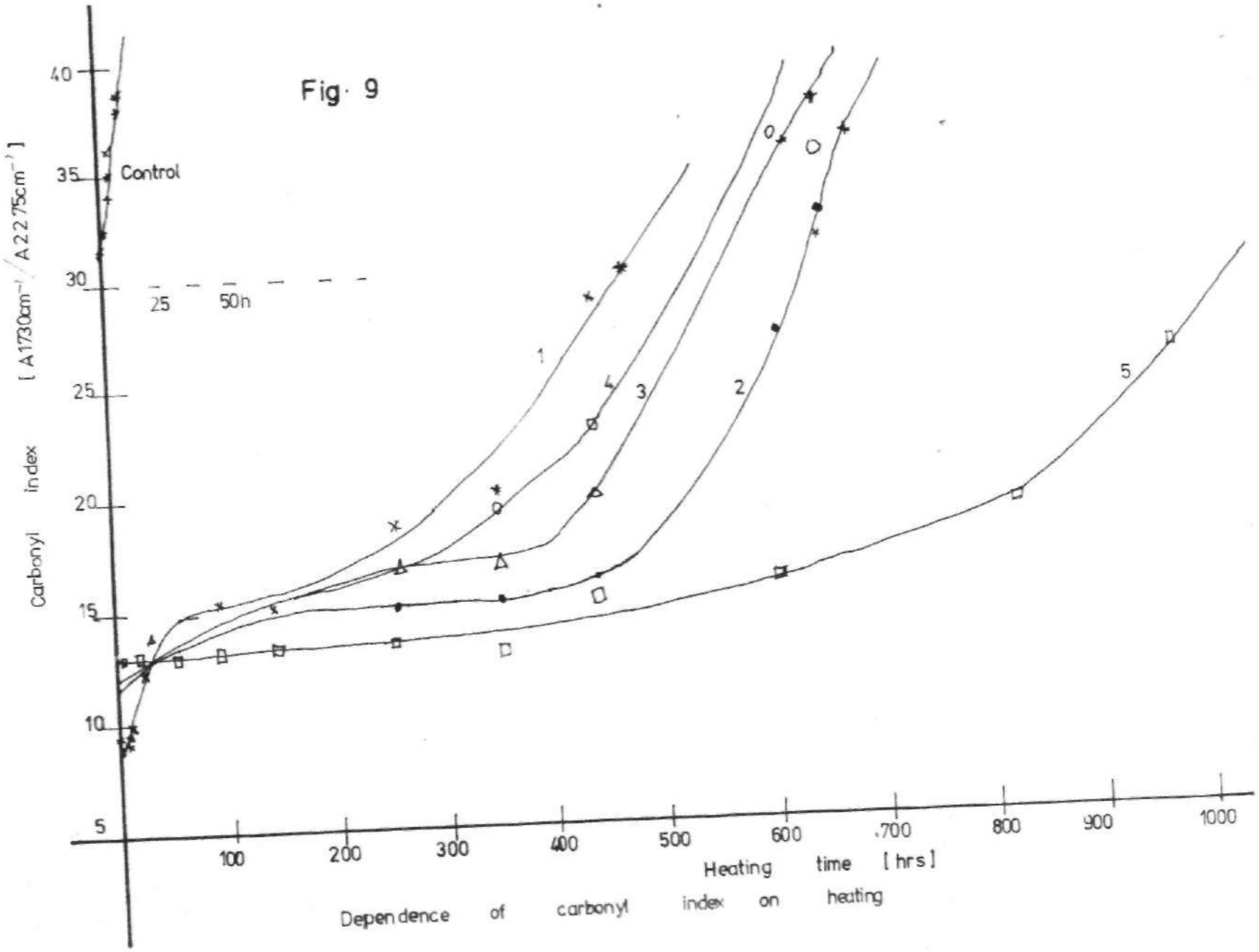


Fig 8 Thermal degradation of ABS

Fig. 9



Dependence of carbonyl index on heating

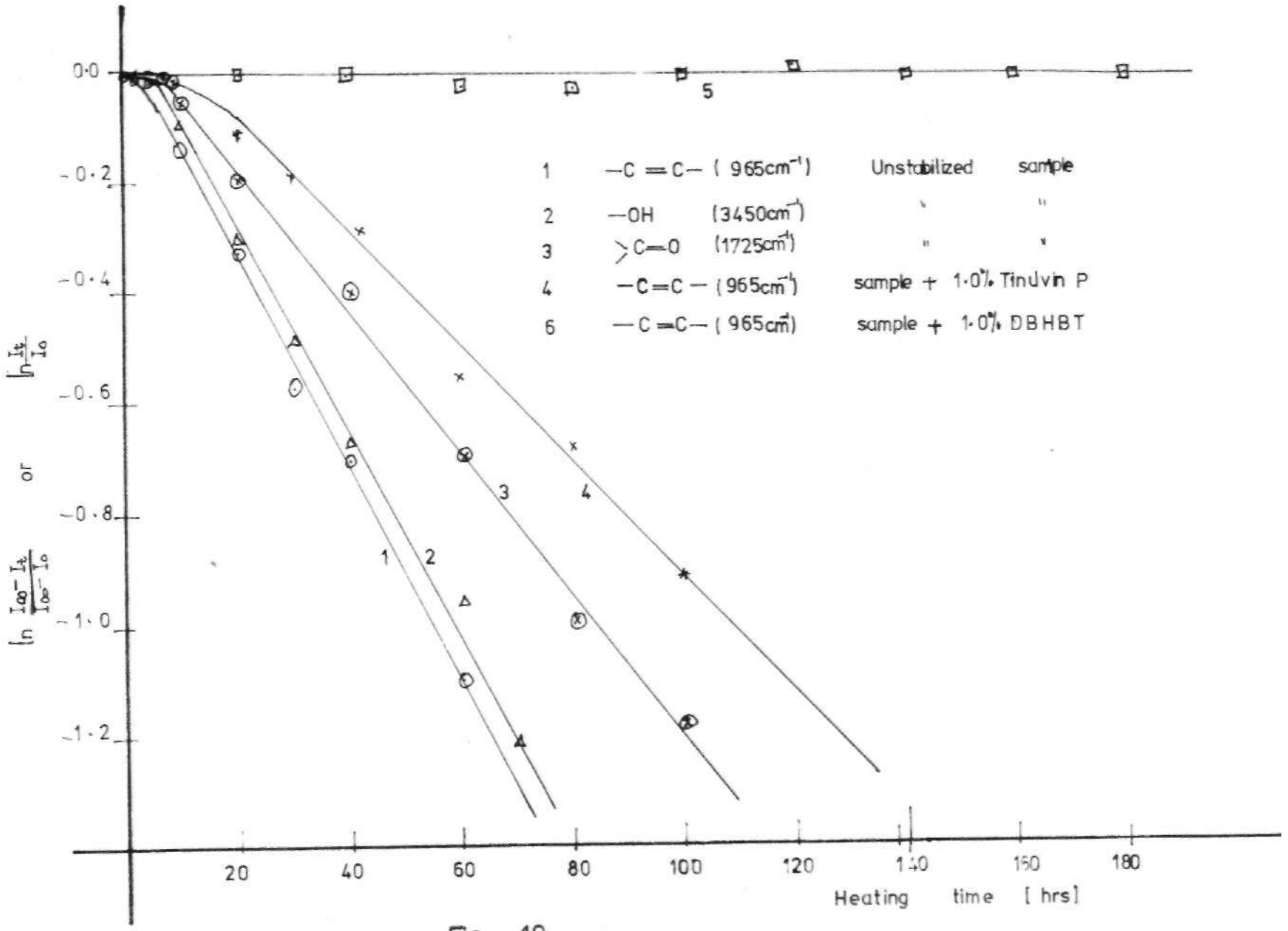

0·0
-0·2
-0·4
-0·6
-0·8
-1·0
-1·2
20
40
60
80
100
120
140
160
180
Heating time [hrs]
or
1 —C ═C— (965cm⁻¹) Unstabilized sample
2 —OH (3450cm⁻¹) " "
3 >C═O (1725cm⁻¹) " "
4 —C═C — (965cm⁻¹) sample + 1·0% Tinuvin P
6 — C ═C— (965cm⁻¹) sample + 1·0% DBHBT
1
2
3
4
5

Fig. 10

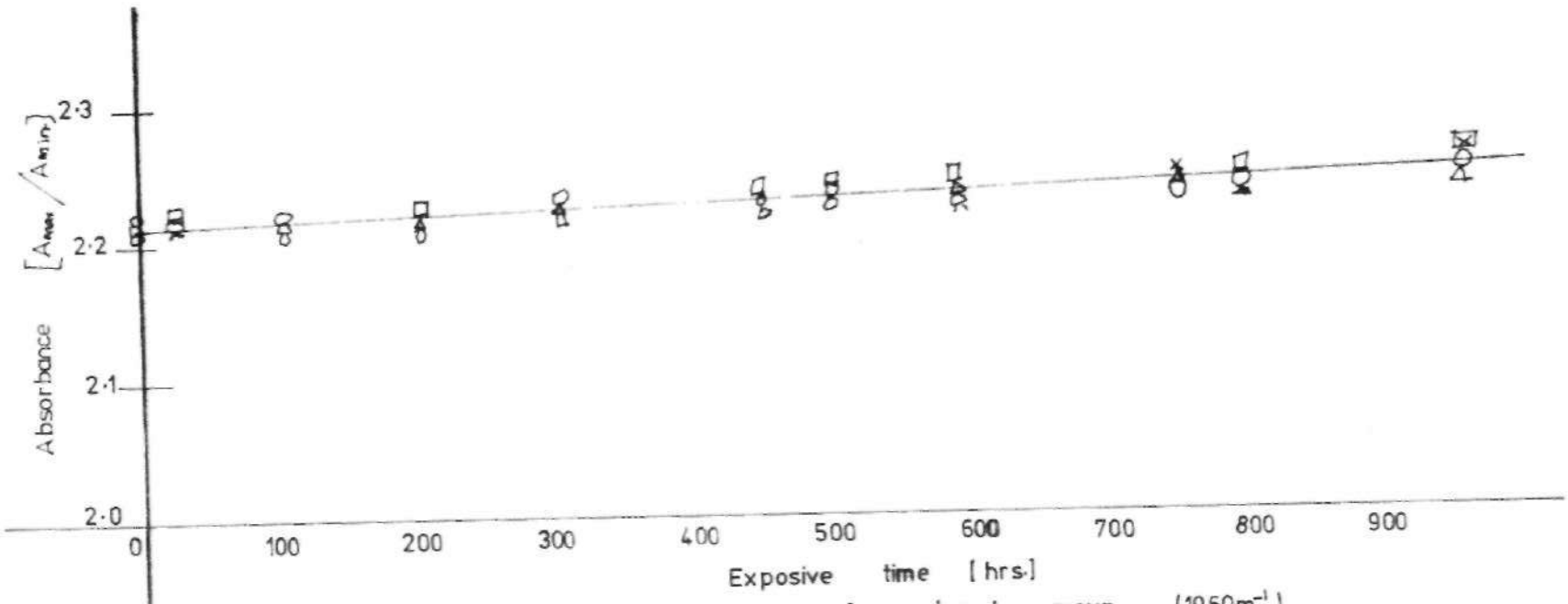


Fig 11a Changes in the absorbance of phenyl group (1960m^{-1})

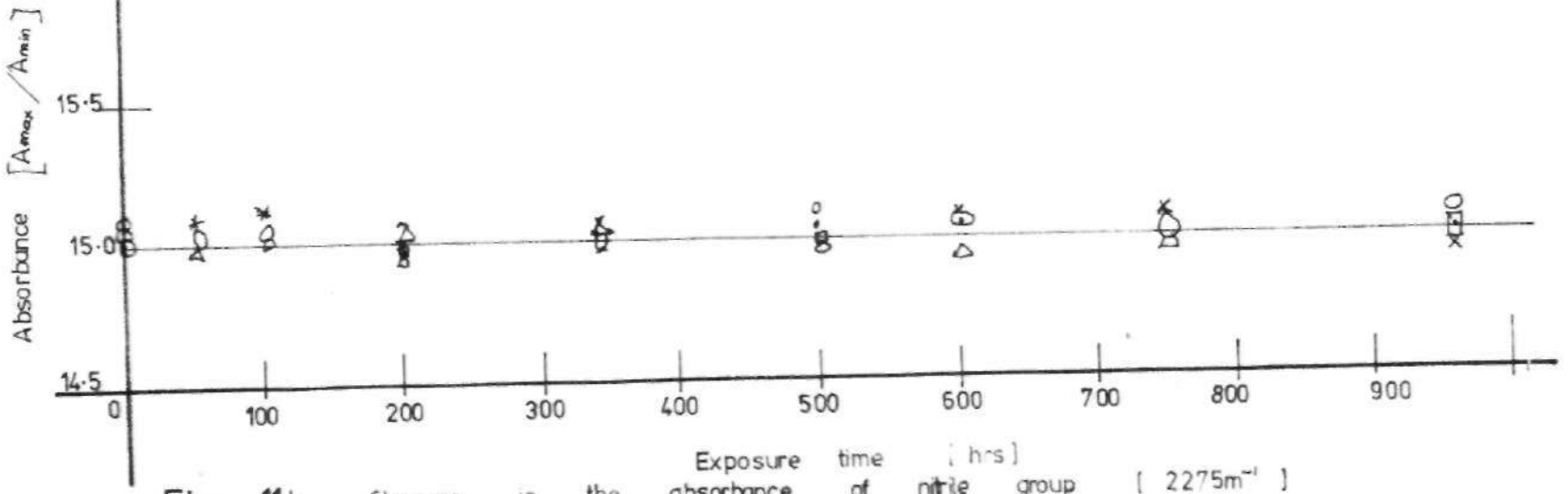
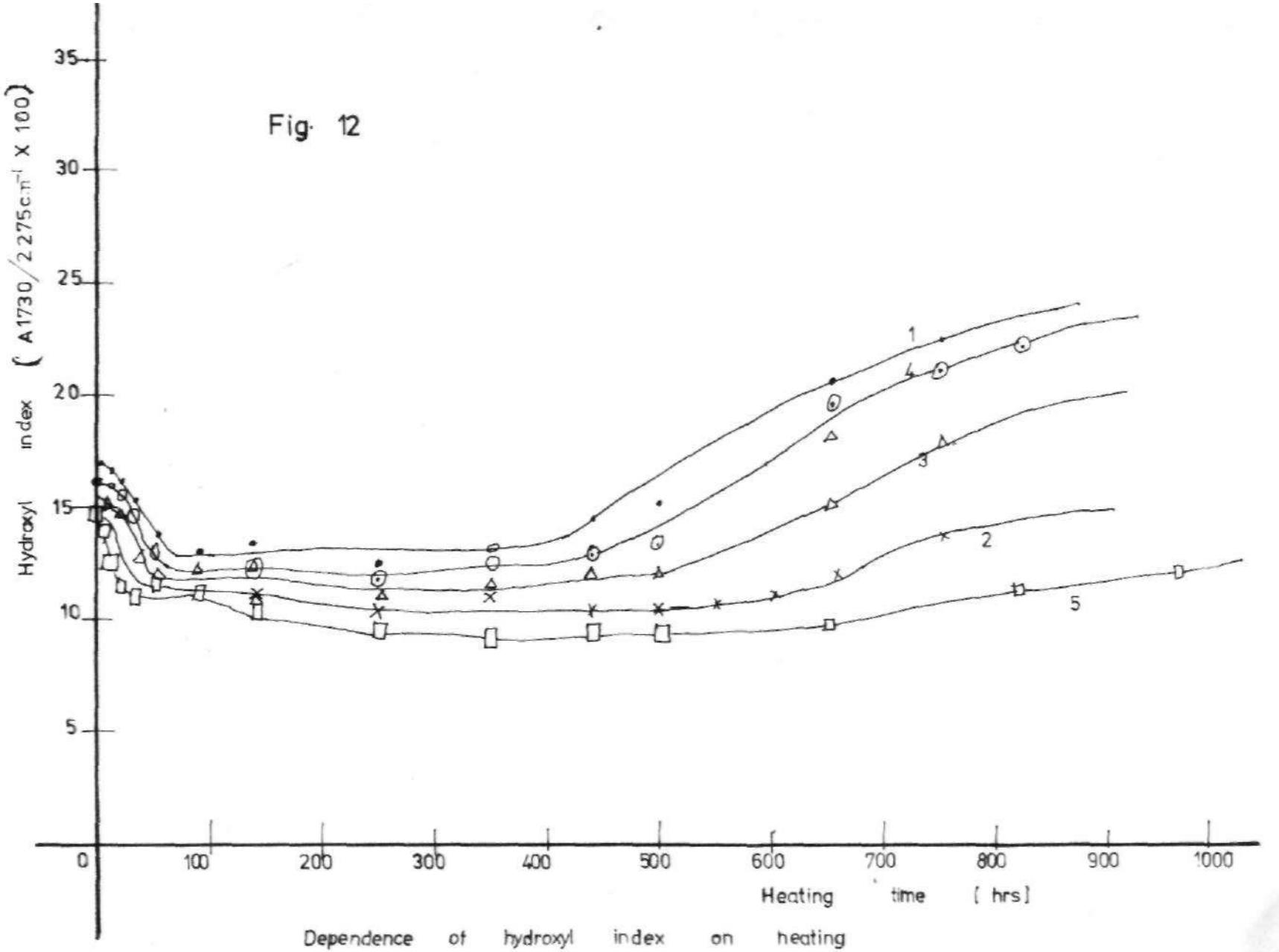


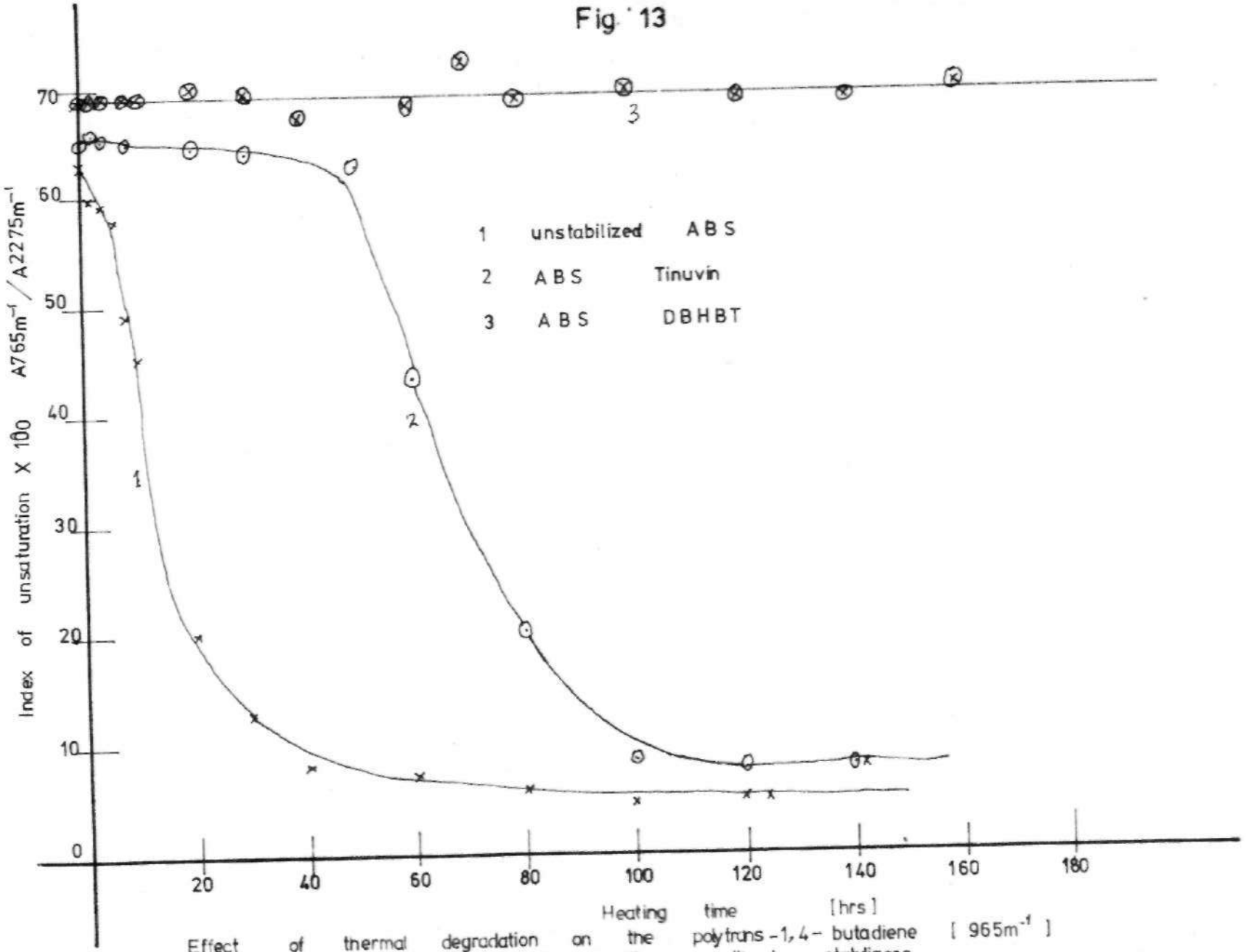
Fig 11b Changes in the absorbance of nitrile group [2275m^{-1}]

Fig. 12



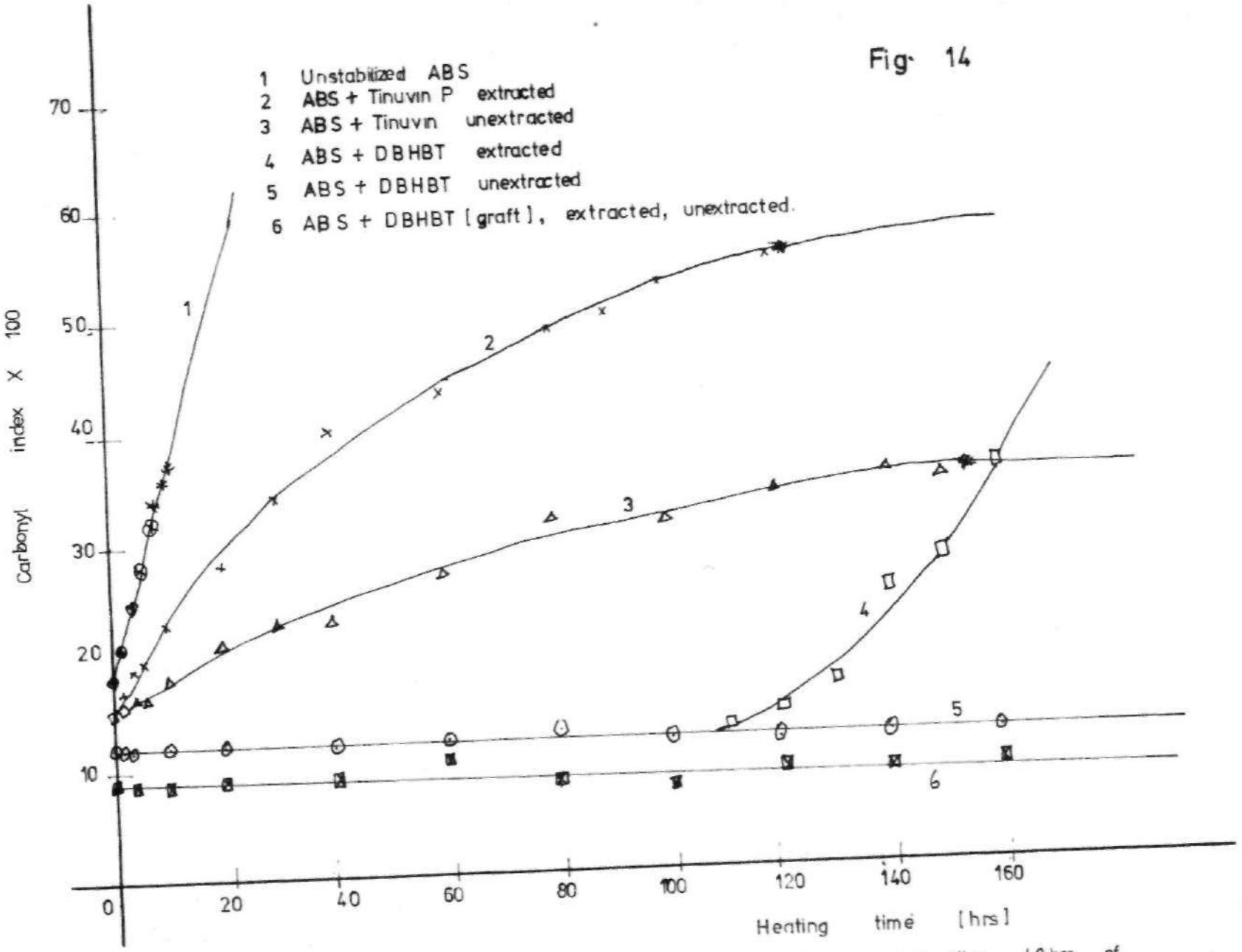
Dependence of hydroxyl index on heating

Fig. 13



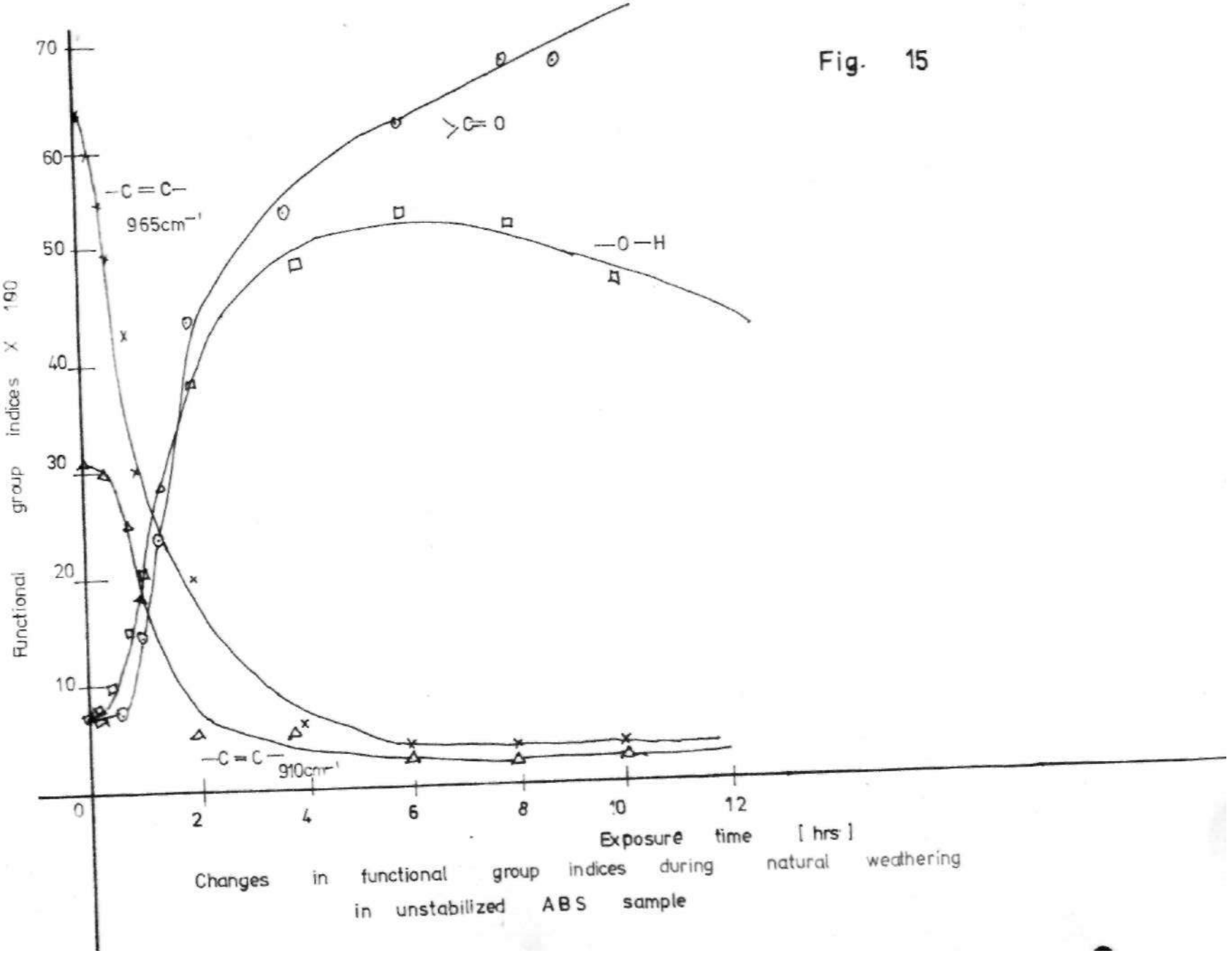
Effect of thermal degradation on the polytrans-1,4-butadiene [965m^{-1}] content of ABS samples with or without stabilizers

Fig. 14



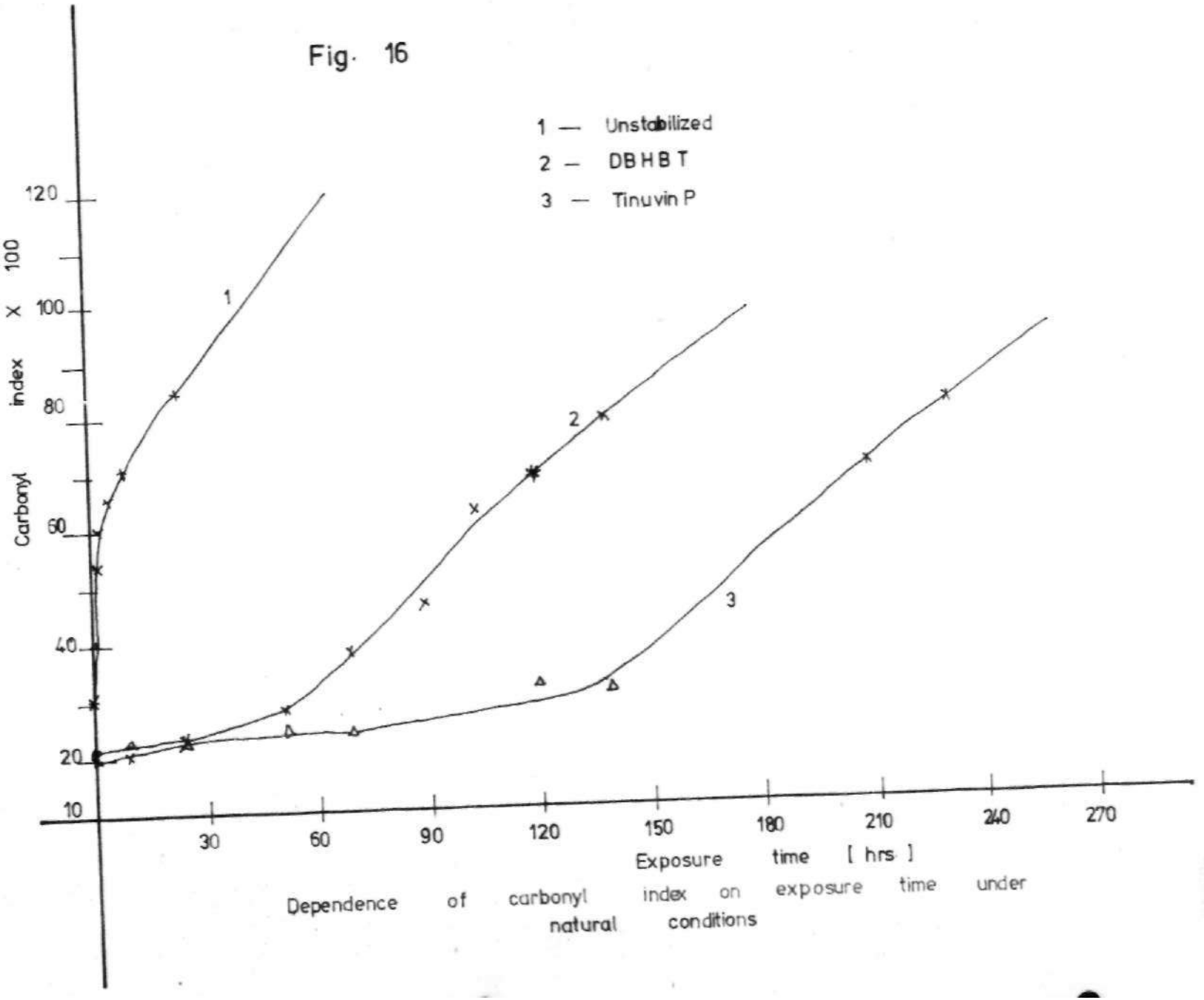
Dependence of carbonyl index on heating before and after 48 hrs of cold extraction in cyclohexane

Fig. 15



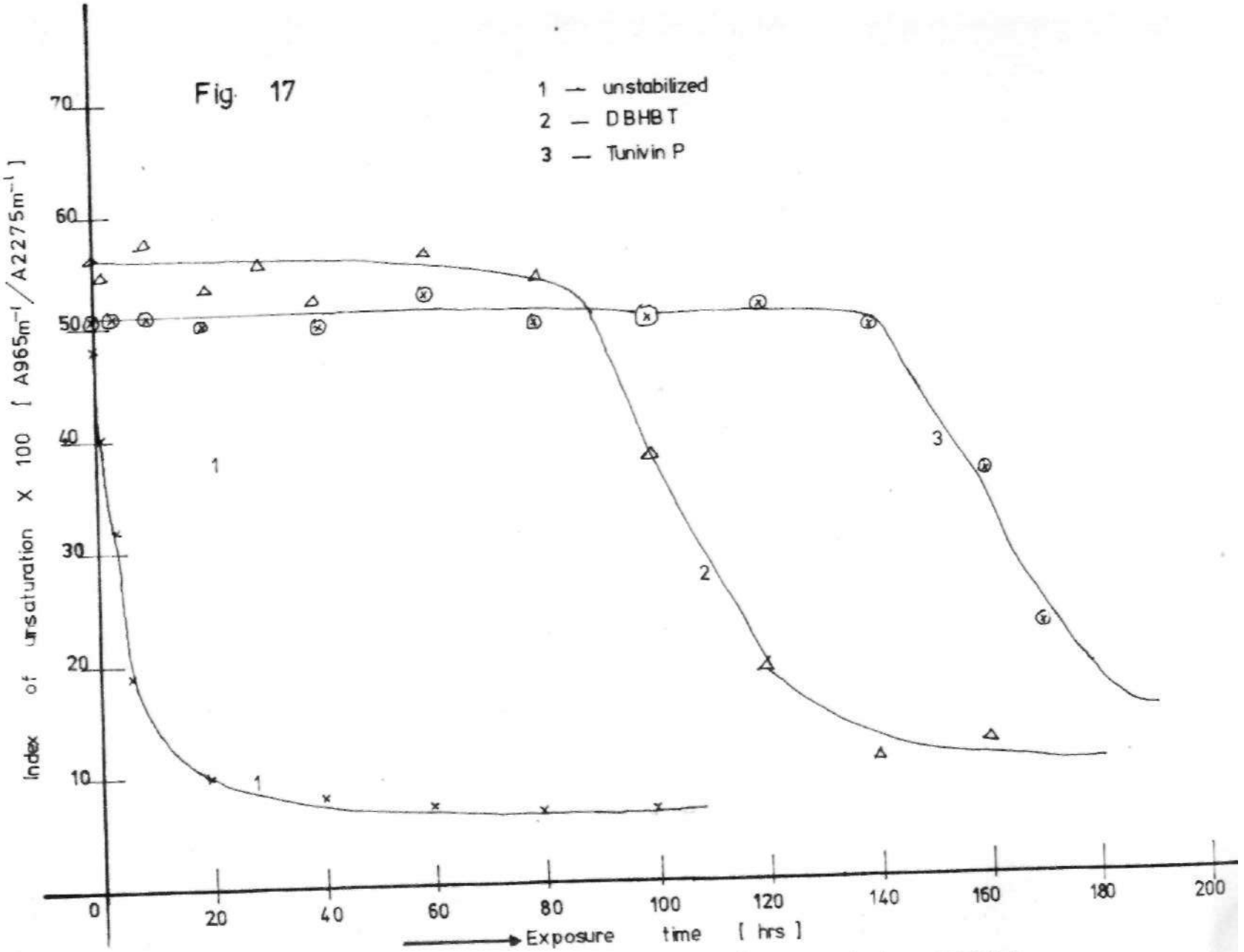
Changes in functional group indices during natural weathering in unstabilized ABS sample

Fig. 16



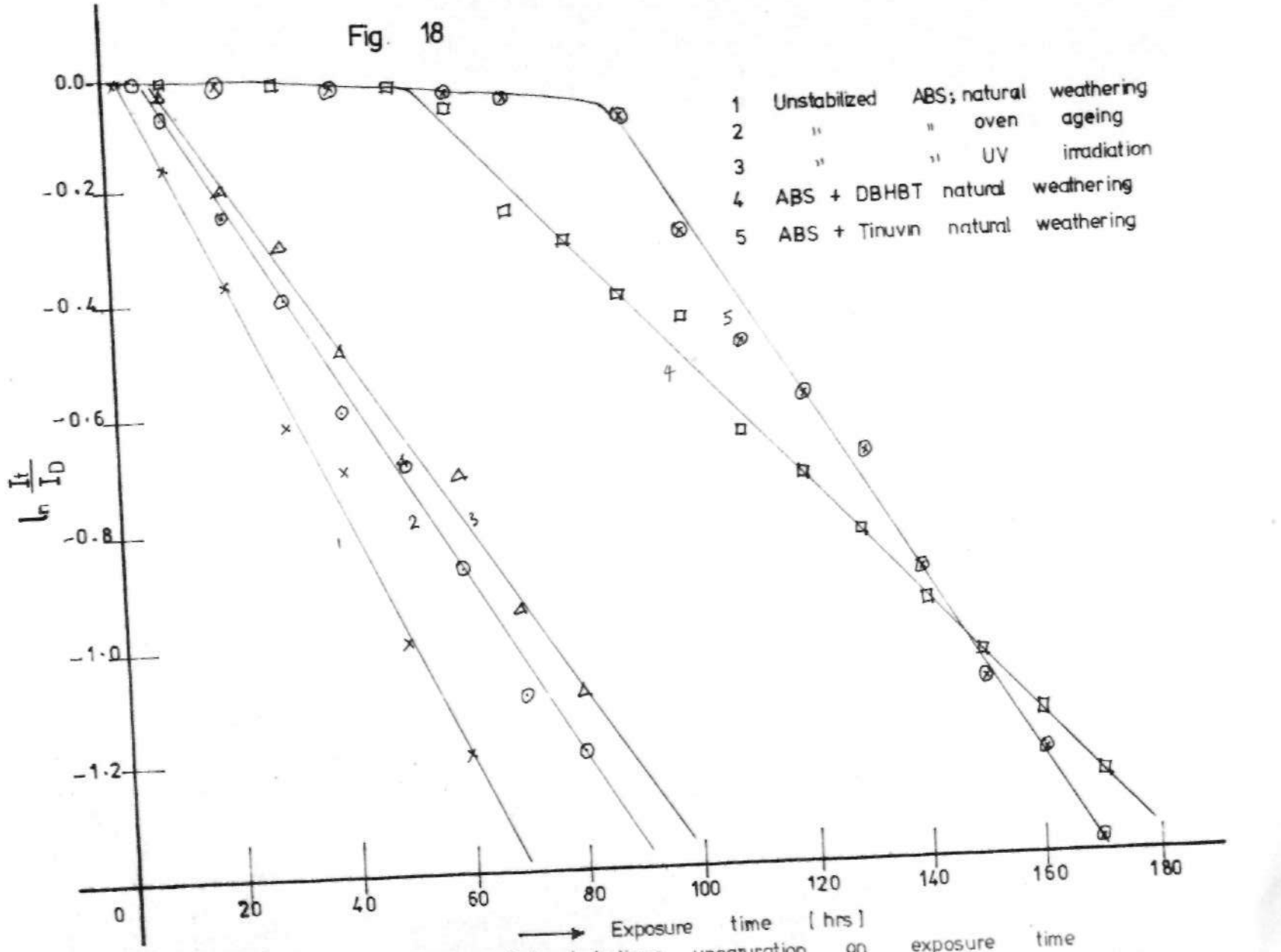
Dependence of carbonyl index on exposure time under natural conditions

Fig. 17



Changes in polytrans — 1, 4 — butadiene during natural weathering

Fig. 18



Dependence of polytrans-1, 4 – butadiene unsaturation on exposure time under various conditions [First – order plots]