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POLYMER-METAL ADHESION PROMOTERS IN UV CURABLE COATINGS

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Different types of acrylic monomers containing functional groups able to improve adhesion on steel substrates were prepared and introduced in a typical UV curable epoxy-acrylic system based on a bisphenol-A-diglycidyl-ether diacrylate with a reactive diluent mixture. The adhesion properties of the films obtained after UV curing were measured and related to the presence of different types of functional groups in the resin. Monomers like esters of phosphoric acid with hydroxy-alkyl-acrylates, adducts of hydroxy-alkyl-acrylates on 2-methyl-2,5-dioxo-1-oxa-2-phospholane, acrylic and methacrylic acids were taken into account. The results obtained show that the adhesion properties depend on the type of functional group present and on the structure of the monomer. Humidity and solvent resistance tests were performed on film containing the additives homogeneously mixed or added as a thin layer on the substrate surface. The results obtained in the different conditions are reported and discussed.

PROMOTEURS DE L'ADHERENCE POLYMERE-METAL DANS DES REVETEMENTS UV-DURCISSABLES

Differents types de monomères acryliques contenant des groupes fonctionnels capables d'améliorer l'adhérence sur des substrats en acier ont été préparés et introduits dans un système époxy-acrylique traitable UV typique, se basant sur un bisphénol-A-diglycidyl-éther diacrylate avec un mélange diluant réactif. Les qualités d'adhérence des films obtenues

après traitement UV ont été mesurées et mises en relation avec la présence de différents types de groupes fonctionnels dans la résine. Il a été tenu compte des monomères tels que les esters de l'acide phosphorique avec les hydroxy-alkyl-acrylates, les additifs de hydroxy-alkyl-acrylates sur 2-méthyl-2,5-dyoxo-1-oxa-2-phospholane, les acides acrylique et méthacrylique. Les résultats obtenus montrent que les qualités d'adhérence dépendent du type de groupe fonctionnel présent et de la structure du monomère. Des tests de résistance à l'humidité et aux solvents ont été effectués sur le film contenant les additifs mélangés de manière homogène ou additionnés comme fine couche sur la surface du substrat. Les résultats obtenus dans ces différentes conditions sont exposés et discutés.

METALL-POLYMER-ADHÄSIONFÖRDERER IN DEN MIT UV BEHANDELBAREN VERKLEIDUNGEN

Verschiedene Typen von acryl-Monomeren bestehend aus funktionellen Gruppen, die in der Lage sind, die Adhäsion auf Stahl-Grundlagematerial zu fördern, wurden vorbereitet und in ein typisch UV-behandelbares Akryl-Epoxy-System auf Bisphenol-A-Diglycidyl-Aether-Diacrylat-Basis zusammen mit einer reaktionsfähigen Verdünnungsmischung eingefügt. Die Adhäsionseigenschaften der nach der UV-Behandlung erhaltenen Filme wurden gemessen und in Beziehung mit dem Vorhandensein von verschiedenartigen funktionellen Gruppen in dem Harz gebracht. Monomeren, wie Ester aus Phosphorsaüre mit Hydroxy-Alkyl-Akrylaten, Zusatzstoffe aus Hydroxy-Alkyl-Akrylaten auf 2-Methyl-2,5-Dioxo-1-Oxa-2-Phospholan, Akryl- und Metakrylsaüren wurden berücksichtigt. Die erzielten Ergebnisse zeigen, daß die Adhäsionseigenschaften von der Monomer-Struktur abhänging sind. Feuchtigkeitswiderstandsprüfungen wurden auf Filmen durchgeführt, die homogen gemischte bzw. als dünne Schicht

auf den Grundlageflächen zugefügte Zusatzstoffe enthalteten. Die unter den verschiedenen Bedingungen erzielten Ergebnisse werden berichtet und besprochen.

1. INTRODUCTION

The increasing importance of radiation curable coatings in different fields like inks, coating of wood, paper, plastics is well established. The great advantages that this technology allows to obtain, have been reported and discussed (1). Some important problems remain open from either the scientific or the technological point of view. It prevents further diffusion and wider applications of this technology. Of particular importance is the control of the properties of the films obtained after radiation curing.

Systematic investigations on the relationships between the properties of the films and the chemical structures of the monomers or oligomers used are necessary for this purpose (2,3) Among the more important properties of these coatings , we can recall the mechanical properties, adhesion to different substrates, protecting characteristics and weathering resistance.

In the case of metallic substrates the adhesion of organic coatings is a difficult problem discussed in some recent reviews (4,5). The simultaneous contribution of chemical bonding, physical bonding and mechanical interlocking is necessary to obtain strong adhesion between organic coatings and metal surfaces.

Mechanical interlocking is obtained by preparing a sufficiently rough microscopic metal oxide surface which favours the penetration of the organic liquid coating prior the curing reaction. Physical bonding is related to the presence of Van der Waals forces between the organic coatings and the metal surface. These forces are very weak and do not provide for durable and stable bonds.

Some hydrogen bonding can also occur between the coating and the oxyde or hydroxide present at the metal surface. Strong adhesion is generally obtained when chemical bonding occurs between the organic coating and the metal oxide at the surface.

For these reasons the most important factors which determine the adhesion of coatings on a metallic substrate are:

1 - surface cleaning and preparation
2 - surface wettability and surface tension of the coating (contact angle of the liquid on the surface)
3 - absence of internal stresses in the coating during the curing reaction or possibility of stress relaxation during curing or after it
4 - specific chemical interactions between the organic coating and the substrate with formation of a chemical bonding.

When UV curable coatings are used, it is the point 3) the most difficult to obtain because of the particular conditions of curing used (low temperature, high curing speed, high volume shrinkage during curing); hence poor adhesion properties result.

The solution to the problem of adhesion of UV curable coatings on metallic substrates, has been undertaken under different points of views (5, 6,7,8):

i - using thermally cured suitable "primers";
ii- introducing thermal treatments before and/or after the UV curing or adopting "dual curing" methods;
iii - using adhesion promoters.

The last methods seems, in principle, the most interesting and also suitable for an easy application.

Generally speaking an adhesion promoter must contain the following groups:

1 - a reactive unsaturation (normally acrylic or methacrylic d.b.) which can copolymeryze with the unsaturations of the coating network;
2 - a functional group able to interact with the metal substrate yielding a chemical bonding;
3 - a spacer group, i.e. a chain segment which links the unsaturation with the functional group, thus making a connection between the two phases. The length and the flexibility of this segment may have a great influence on the behavior of the adhesion promoter (9).

Some acidic acrylates (10) have been reported as adhesion promoters on metallic substrate in the patent literature but no scientific paper has yet been published on this argument.

In this work different acrylic compounds containing acidic groups in the molecule, were prepared and tested as adhesion promoters on steel substrates in the presence of a typical UV curable epoxy-acrylic resin.

Two classes of functionalized monomers were prepared, and tested, namely (i) acrylic or methacrylic compounds containing carboxylic groups, (ii) esthers of phosphoric acids with hydroxy-alchyl-acrylates. In this manner monomers containing - COOH, $-\mathrm{P}\begin{smallmatrix}\mathrm{OH}\\ =\mathrm{O}\\ \mathrm{OH}\end{smallmatrix}$ or $=\mathrm{P}\begin{smallmatrix}\mathrm{OH}\\ =\mathrm{O}\end{smallmatrix}$ as pendant groups were considered.

The films obtained after UV curing of the different mixtures were evaluated and compared with the films obtained with the reference resin: curing characteristics, adhesion properties, humidity and solvent resistence were examined.

2. EXPERIMENTAL

2.1. Materials

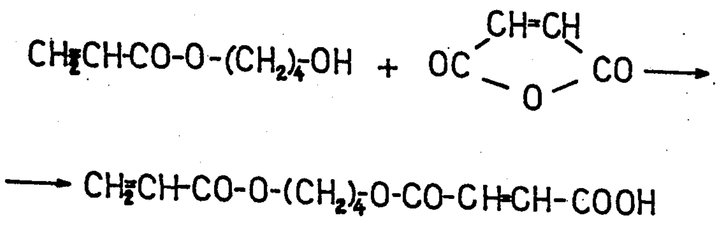
As a reference UV curable resin, a typical epoxy-acrylic resin (BGEDA) was used (Ebecryl 605 from U.C.B.) containing bisphenol-A-diglycidyl-ether-diacrylate and a reactive diluent (tri-propylene-glycol-diacrylate) in 75/25 weight ratio.

Commercial grade acrylic acid (AA), methacrylic acid (MA), 2-hydroxy-ethyl-acrylate, 4-hydroxy-butyl-acrylate, 2-methyl-2,5-dioxo-1-oxa-2-phospholane (from Hoechst) were used as received.

As photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Irgacure 651 from Ciba Geigy) was used.

A number of acrylic compounds containing functional groups were prepared according the following reactions.

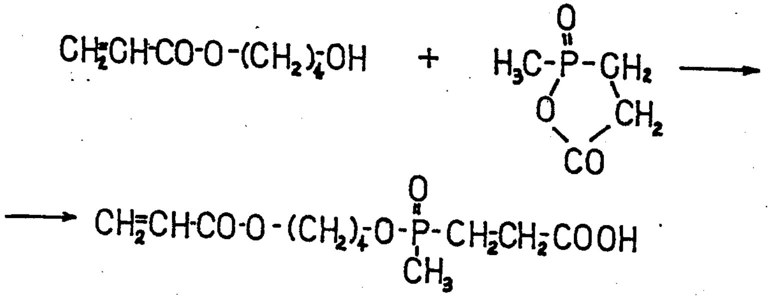
Mono-4-(acryloyloxy)-butyl maleate (ABM) was obtained by reacting 4-hydroxy-butyl-acrylate with maleic anhydride at 70°C in benzene solution according to the scheme reaction:



The IR spectrum of the obtained product is reported in Fig.1.

Mono-2-(acryloxy)-ethyl maleate (AEM) was prepared similarly by reacting 2-hydroxy-ethyl-acrylate with maleic anhydride.

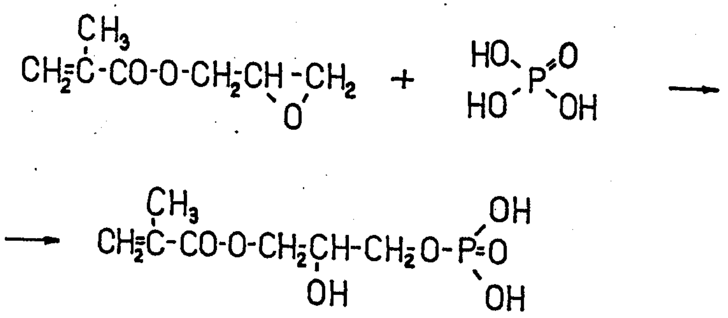
The adduct of 2-methyl-2,5-dioxo-1-oxa-2-phospholane with 4-hydroxy-butyl-acrylate (FBA) was obtained by reacting the components at room temperature according to the scheme reaction:



which takes into account the main product as identified by IR analysis (Fig. 2) and the results reported in the literature (11, 12).

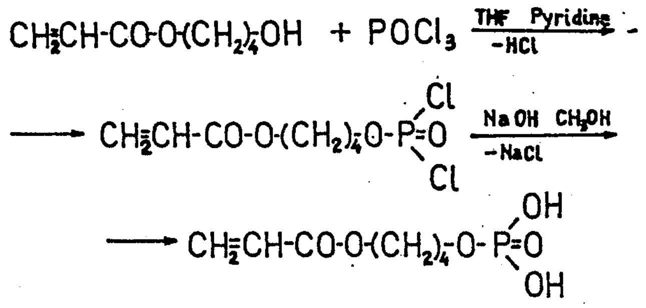
The adduct of 2-methyl-2,5-dioxo-1-oxa-2-phospholane with 2-hydroxy-ethyl-acrylate (FEA) was prepared in the same manner.

Mono-2-hydroxy-3-(methacryloyl-oxy)-propyl-phosphoric acid (HMPF) was prepared by reacting glycidyl-methacrylate with phosphoric acid at room temperature according to the scheme:

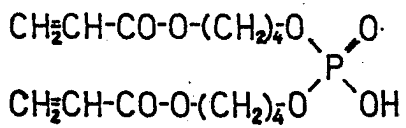


The IR spectrum of the obtained product (50% b.w. solution in 2-hydroxy-ethyl-acrylate) is reported in Fig. 3.

Mono-4-(acryloyl oxy)-butyl-phosphoric acid (MABF) was obtained by reacting 4-hydroxy-butyl-acrylate with $POCl_3$ according to the followings scheme:



The IR spectrum of the obtained product is reported in Fig.4.
In the same manner by changing the molar ratio of the reagents di-4-(acryloyl-oxy)-butyl-phosphoric acid (DABF) was prepared.



The obtained products were characterized by IR, H^1-NMR, elemental analysis and potentiometric titrations. The details of the syntheses will be reported in a forthcoming paper (13).

2.2. Curing

Sheets of cold-rolled mild steel were used as substrates;they were sanded, rinsed with a solvent and stored in a desiccator before use:
The formulations containing 5% b.w. of photoinitiator, were applied on the sheets with a calibrated wire wound applicator to obtain a tickness of about 50 µm and irradiated by using a 500 W medium pressure mercury lamp (Helios Italquarz) at a distance of 20 cm, in an air atmosphere. In some experiments a N_2 atmosphere was used. The samples were irradiated until a constant maximum value of hardness was reached. In some cases a double layer coating was prepared containing a thin layer of the additive applied with a cylindrical rod (~ 3 µm) and a layer of the BGEDA resin with the calibrated applicator (~ 50 µm).
The kinetics of curing was followed by IR measurements (FTIR Bruker IFS45 Instr.) on thin films coated on KBr discs by following the decrease of the IR bands at 1635 and 1410 cm^{-1} due to the acrylic d.b. present in the resin. An experimental device similar to that previously reported (14) was used.
In all the experiments samples containing a definite amount of the different additives were compared with the pure BGEDA resin and the different behaviour was evaluated.
An amount of 10 mmoles of the additive for 10 g of BGEDA resin was normally used: in some cases half of the additive concentration was used.

2.3. Testing Methods

On the samples irradiated pencil hardness and thickness measurements with a magnetic gauge were performed.
The adhesion properties were evaluated by two methods:
- cross-hatching test (DIN 53151) making the cross-cut incision followed by tape test.

- pull-off test by measuring the pull-off force with a dinamometer (J. and J. Instr;, T5K) by using Aluminium cylinders glued on the coating surface by means of Araldite adhesive (5).

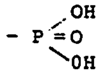
The humidity resistance of the cured samples was determined by salt fog exposure (ASTM B-117) and humidity cabinet exposure (95% rh., T = 40°C);

Solvent resistance was evaluated at room temperature by placing drops of different chemicals on the film, covering them with a watch glass and noting the effect after 24 hrs.

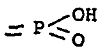
All the measurements were performed when the samples were stored for a minimum of 48 hrs after curing.

3. RESULTS AND DISCUSSION

The choice of the functionalized monomers has been performed in order to have within the molecule different acidic groups and different structures. Namely the presence of - COOH,



$-P(=O)(OH)_2$



$=P(OH)=O$ groups was taken into account.

The prepared monomers were added to the BGEBA resin and the properties of the films obtained after UV curing were evaluated. First the influence of the monomers on the kinetics of UV curing was considered subsequently the adhesion properties and the humidity and solvent resistence of the films coated on steel substrates were determined; In all cases the properties were compared with those of the films containing pure BGEDA resin.

3.1. Kinetics of curing

Fig. 5 shows kinetic curves relative to the unsaturation disappearance under UV irradiation of films obtained from pure BGEDA resin and mixtures with FBA or MABF (conc.= 5 mmoles/ /10 g). It can be seen that there is a decrease in the curing

rate in the presence of the additives, mainly MABF. Such a poisoning effect may be associated to the interaction of the radicals with the additives used and will be further discussed in a forthcoming paper (13).

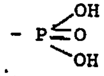
It can be noted that this effect can influence the properties of the films after UV curing, particularly the adhesion characteristics. Thus it must be taken into account in the interpretation of the properties of the obtained products.

3.2. Adhesion properties of the coating

Table 1 collects the results of adhesion measurements of films from pure BGEDA resin and its mixtures with the different functionalized monomers coated on steel substrates. Both cross-hatching and pull-off tests show that the adhesion increases in the presence of the additives and the effect increases in the order:

$$AA \simeq MA < AEM \simeq FEA < ABM \simeq HMPF \simeq DABF \simeq FBA < MABF$$

The strongest interaction with the steel substrate is obtained by using the monomer containing



$-P(=O)(OH)_2$ groups followed by FBA, DABF and HMPF monomers. In all cases the presence of a chain segment with an increased length and flexibility between the acidic function and the acrylic d.b. increases the adhesion of the film.

3.3. Humidity and solvent resistance

In Table 2 results of some salt fog exposure tests of films from pure BGEDA resins and its mixtures with MABF and FBA on steel substrates are reported. It can be noted that, after 100 hrs. exposure, adhesion disappears in any case. This fact means that the adhesion bonds are humidity sensitive (15,16). Moreover the films containing the additives show poor surface aspect and blistering.

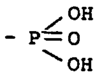
These results evidence the problems connected with the presence of hydrophilic groups in the resin network; in fact they reduce the water resistance of the film. The problem can be in part overcome by using a double layer coating, constituted by a thin layer of the additive and an upper layer of pure BGEDA resin, as shown in Table 2.

Similar results are obtained from the humidity resistance tests after 50 and 100 hrs exposure, as reported in Table 3.

Finally in Table 4 results of the solvent resistance of the different coatings after UV curing are listed. They show that the solvent resistance is generally good; only in the case of the MABF and ABM additives a lower solvent resistance is observed .

It has to be further noted that, by curing the coatings in N_2 atmosphere, the solvent resistance is in any case increased.

4. CONCLUSIONS

The use of additives containing specific acidic groups in the molecule can increase sharply the adhesion of a typical epoxy-acrylic resin on a steel substrate; The strongest bonding is obtained in the presence of monomers containing  $-P(=O)(OH)_2$ groups. Also the structure of the monomer is important and the adhesion increases by increasing the length and flexibility of the chain segment connecting the acidic group to the unsaturation in the monomer.

Sometimes also the kinetics of the curing reaction is changed in the presence of the additive and this fact makes difficult the interpretation of the results. In any case, a humidity sensitive chemical bonding with the steel substrate is obtained using these types of additives. Furthermore the humidity resistance of the coating is decreased by the presence of the hydrophilic groups contained in the molecules of the tested monomers.

Acknowledgements:

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Table 1 - Results of adhesion measurements through cross-hatching and pull-off tests (thickness: 50 μm; conc. of the additive = 10 mmole/10 g).

Additive type	Cross-hatching (%)	Tape adhesion (%)	Pull-off test (N/cm^2) *
-	40	0	25 ± 6
AA	50	0	28 ± 12
MA	50	0	52 ± 14
ABM	100	80	185 ± 36
AEM	60	0	75 ± 22
FBA	100	80	215 ± 32
FEA	60	0	68 ± 12
HMPF	100	40	190 ± 22
MABF	100	100	280 ± 32
DABF	100	30	165 ± 35

* Mean of 5 determinations and standard deviation.

Table 2 - Results of salt fog test of coatings from BGEDA resin and its mixtures with MABF and FBA (100 hrs exposure; thickness = 50 micron; conc. of the additive = 10mmole/10 g).

	General Aspect a)	Adhesion Cross-hatching	Tape adhesion
BGEDA	G	0	0
BGEDA - MABF	IS	0	0
BGEDA - MABF b)	G	100	100
MGEDA - MABF c)	G	95	0
MGEDA - FBA	IS	0	0
BGEDA - FBA d)	S	40	0
BGEDA - FBA e)	IS	0	0

a) General surface aspect and blistering:
G = good; S = sufficient; IS = insufficient

b) = double layer coating: pure MABF (3 μm) and pure BGEDA resin (50 μm)

c) = double layer coating: BGEDA - MABF (3 μm) and pure BGEDA resin (50 μm)

d) = double layer coating: pure FBA (3 μm) and pure BGEDA resin (50 μm)

e) = double layer coating: BGEDA - FBA (3 μm) and pure BGEDA resin (50 μm).

Table 3 - Results of humidity resistance test of coatings from BGEDA resin and its mixtures with MABF and FBA.(*)

		General Aspect	Adhesion Cross-hatching	Tape adhesion
BGEDA	50 hrs	G	0	0
	100 hrs	G	0	0
BGEDA-MABF	50 hrs	S	90	30
	100 hrs	IS	0	0
BGEDA-FBA	50 hrs	S	0	0
	100 hrs	IS	0	0

(*) Symbols and conditions as in Table 2.

Table 4 - Solvent resistance of coatings from BGEDA resin and its mixtures with functionalized monomers. (*)

	n.Heptane	Toluene	1-Butanol	Methyl-isobutyl-ketone
BGEDA	G	G	G	G
BGEDA-AA	G	G	G	G
BGEDA-ABM	G	G	G	S
BGEDA-FBA	G	G	G	G
BGEDA-HMPF	G	G	G	G
BGEDA-NABF	G	G	S	S
BGEDA-DABF	G	G	G	G

(*) Symbols and conditions as in Table 2.

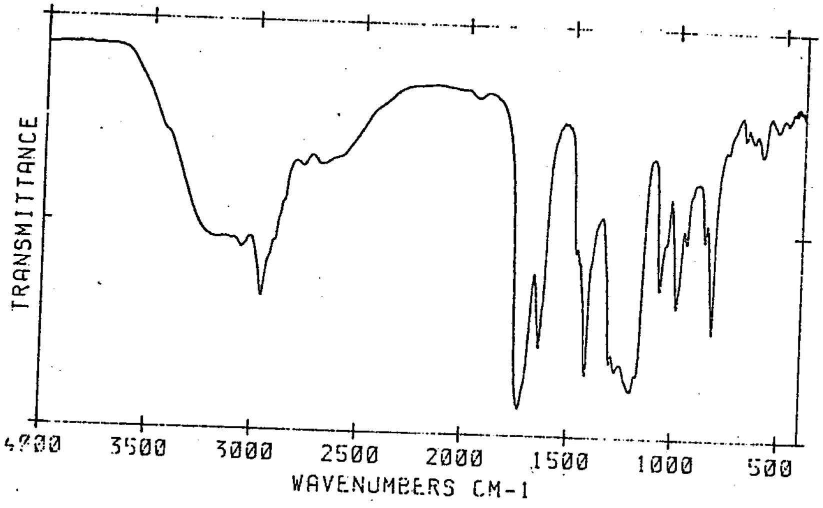

Fig. 1 - FT.IR spectrum of mono-4-(acryloyl-oxy)-butyl maleate (ABM).

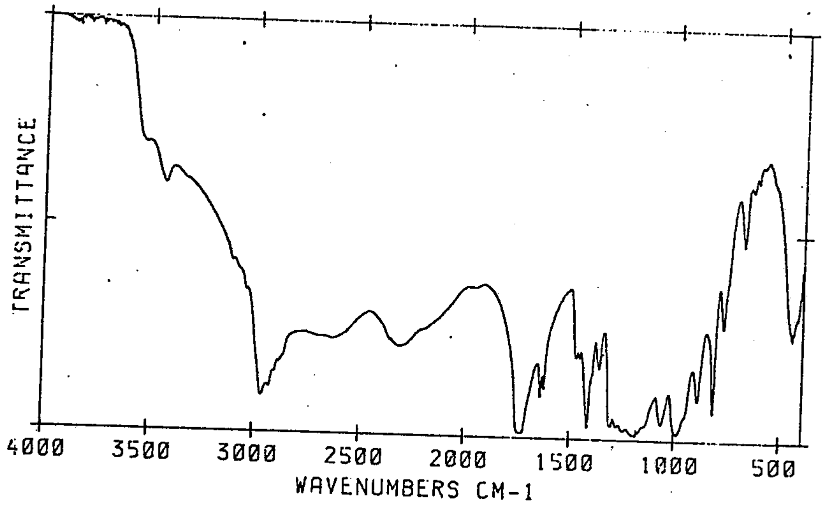

Fig. 2 - FT.IR spectrum of adduct of 2-methyl-2,5-dioxo 1-oxa-2-phospholane on 4-hydroxy-butyl acrylate (FBA).

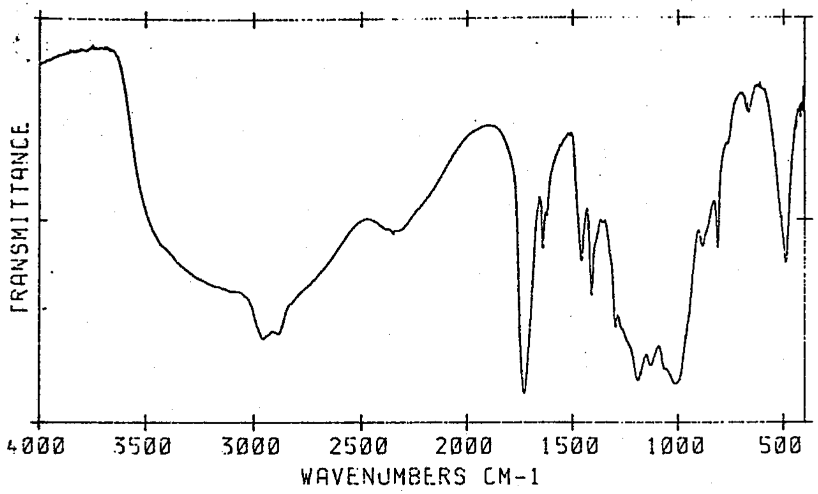

Fig. 3 - FT.IR spectrum of mono-2-hydroxy-3-(methacryloyl - oxy)-propyl-phosphoric acid (HMPF), 50% b.w.solution in 2-hydroxy-ethyl-acrylate.

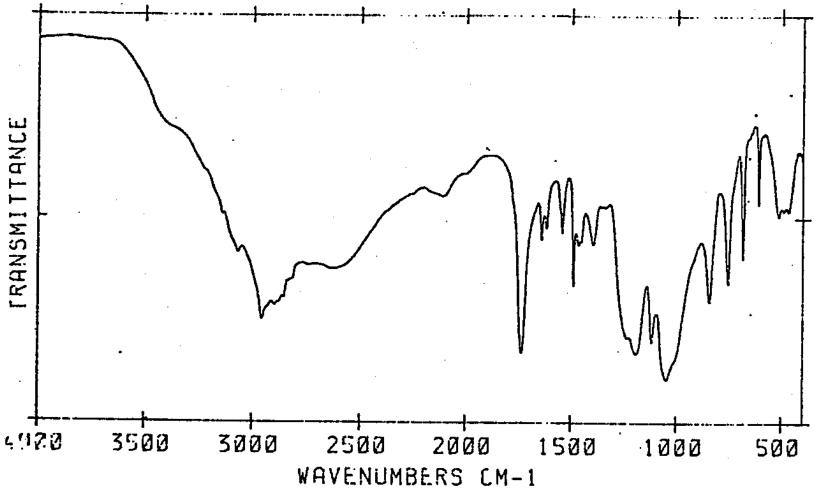

Fig. 4 - FT.IR spectrum of mono-4-(acryloyl-oxy)-butyl-phosphoric acid (MABF).

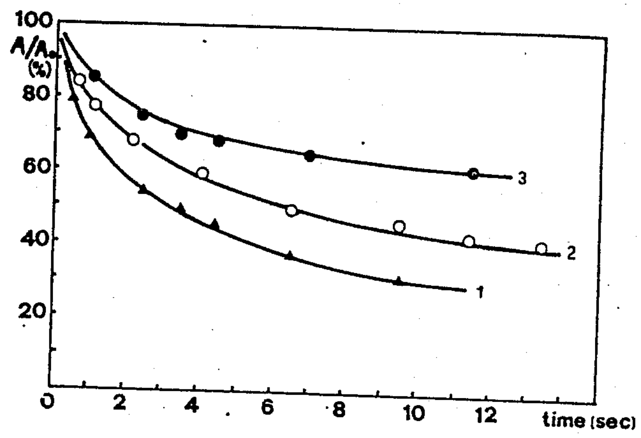

Fig. 5 - Kinetic curves pertaining to BGEDA resin (1) and mixtures with FBA (2) and with MBAF (3). Ratio of the absorbances at 1635 cm^{-1} vs. the irradiation time. (Conc. of FBA or MBAF = 5 mmole/10 g).