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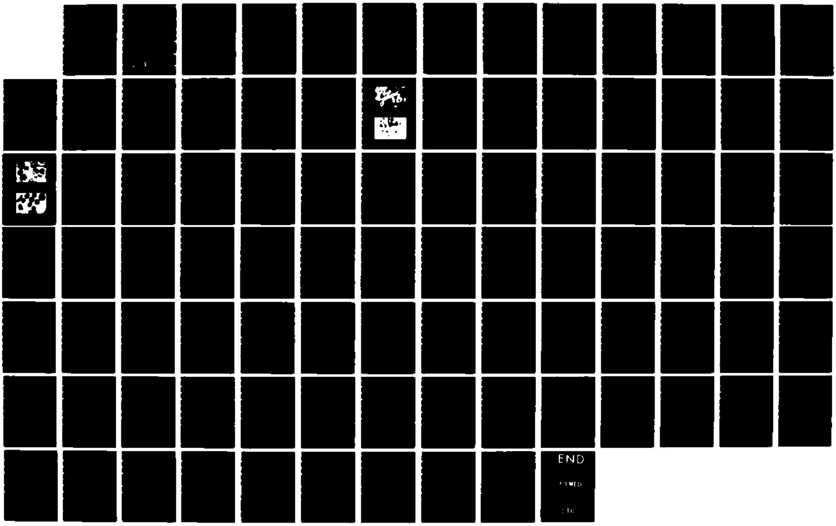

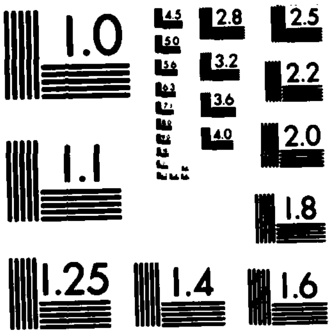

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DEVELOPMENT OF CAPSULAR ADHESIVE SYSTEMS AND EVALUATION OF THEIR STABILITY.

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During the initial phase of this program, studies on microencapsulation of adhesive systems were conducted in which the capsule shells are made from the own encapsulated material. Encapsulation trials were conducted on anaerobic adhesives and epoxy resins. The resulting capsular adhesives were characterized. Comparative adhesion tests were performed with encapsulated and unencapsulated systems.

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LaRell K. Smith

LARELL K. SMITH, Major, USAF
Chief, Physics/Physical Chemistry

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SECTION I

INTRODUCTION

This report describes the research conducted during a one year extension of the contract for the Development of Capsular Adhesive Systems and Evaluation of their Stability, included into the Program for the Study of Aerospace Materials, Coatings, Adhesions and Processes, partially granted by the Air Force Office of Scientific Research, USAF, Grants AFOSR-82-0346 and AFOSR-83-0340.

During the initial phase of this program (1), studies on microencapsulation of adhesive systems were conducted in which the capsule shells are made from the encapsulated material itself, by means of controlled homopolymerization processes at the surface of single droplets of the foresaid adhesive systems. Encapsulation trials were carried out on anaerobic adhesives and epoxy resins. In the case of anaerobic adhesives, two commercial products based on dimethacrylate esters: Loctite 270 and Loctite 290 were encapsulated by promoting an "in situ" homopolymerization at the surface of discrete droplets formed into aqueous medium by means of vigorous agitation with magnetic stirrer or by injection through syringe needles, and therein contacted with an appropriate polymerization catalyst such as sodium bisulphite or a Redox system for a sufficient period of time to permit formation of an encapsulating shell with the thickness required to provide capsules with

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(1) "Development of Capsular Adhesive Systems and Evaluation of their Stability". Final Sci. Report, 10 November 1983, Project EOARD 82-057. Task 2301/D1. European Office of Aerospace Research and Development. London.

acceptable handling properties. The effect of operating conditions on capsules characteristics was determined by performing different runs with controlled variations in experimental conditions. With appropriate procedures stable capsules with size ranges between 50 and 1200 microns and core active contents varying from 75 to 90% were obtained.

For microencapsulation trials of epoxy resins, a low viscosity liquid DGEBA resin: Bepox LX/21 was chosen. The technique used was centrifugal spraying and allowing the discrete droplets to fall into a hardening bath in which a mixture of BF_3 etherate and water was used as polymerization catalyst. The effect of experimental parameters (mainly sprayhead rotation speed, catalyst concentration and hardening time) on capsules characteristics was evaluated. Capsules with size ranges between 100 and 1200 microns and active content from 75% to 88% were obtained. Heat curable capsular adhesive systems were developed with a physical form of free flowing granulate by mixing epoxy capsules with a solid hardener, methylenedianiline (MDA).

A number of lap shear tests were carried out for comparative evaluation of bonding strengths with encapsulated and unencapsulated adhesives. With the encapsulated epoxy system bond strengths of about 70% from the original values (unencapsulated) were achieved, with a curing schedule of 4 hours at 90ºC + 8 hours at 140ºC. Adhesion tests with Loctite adhesives proved that a hardening schedule of 24 hours at room temperature (between 20ºC and 25ºC) was insufficient to provide a complete hardening and gave low bond strengths for both encapsulated and unencapsulated systems, whereas with a curing schedule of 20 hours at 75ºC comparable or even higher bond strength values were obtained with encapsulated systems with regard to the original unencapsulated adhesives.

Finally, characterization studies were performed on raw materials in which several physico-chemical properties have been measured. Infrared spectroscopy was also used for identification and characterization purposes. It was found that computerized difference spectra from cured to uncured adhesives is a useful tool in order to detect and follow the chemical or structural changes involved in curing or ageing processes.

Following the final recommendations of the previous Report, the work carried out during the program extension has been directed towards the completion of the studies initiated in the initial phase of this program. The efforts have been concentrated in the following areas:

1 - Additional microencapsulation trials with epoxy resins and anaerobic compositions with other hardening catalysts and improved control of the operating conditions or some modification of the adhesives, e.g. incorporating some additives in order to improve the capsules handling and stability characteristics.

2 - Fulfilment of complementary adhesion tests with both encapsulated and unencapsulated systems with other types of adherents in order to confirm or modify the initial results.

3 - Forthgoing studies towards the development of capsular epoxy adhesive formulations with improved homogeneity by anchoring the curing agent on the outside surface of the capsules.

4 - Determination of long term capsular systems stability relative to humidity, light and temperature storage limitations and besides variations in bonding properties of artificially aged capsular systems.

5 - Accomplishment of further characterization studies on raw materials and adhesives formulations in order to detect and follow the chemical or physical changes associated with the advancement of polymerization in curing or ageing processes. For this purpose, liquid chromatography (HPLC and GPC) has been used as main analytical technique in addition to computerized infrared spectroscopy initially used.

The work conducted to achieve the objectives listed above is presented in the following sections.

SECTION II

TECHNICAL DISCUSSION

Since the work carried out during the program extension covers different study areas, this Section will be structurated accordingly with the key topics outlined in Section I, which can be listed as follows:

A - Complementary microencapsulation studies with epoxy resins and anaerobic compositions.

B - Trials for development of capsular epoxy adhesive systems with anchorage of the hardener on the capsules surface.

C - Capsules stability studies under various conditions, humidity, temperature, ultraviolet radiation, etc.

D - Bonding studies with capsular systems in order to asses their functionality and retention of adhesion properties after ageing processes.

E - Chemical characterization of raw materials and capsular adhesives by using liquid chromatography and infrared techniques in order to correlate physical and adhesive variations caused by ageing processes with chemical changes in those compositions.

The work conducted into each particular item is presented separately in this Section.

A - Complementary microencapsulation studies.

The experimental work conducted during the initial phase of this program on microencapsulation of anaerobic compositions and epoxy resins has been completed in this period with additional trials, in which the same materials and encapsulation techniques have been basically used, as described in the former report (1), but introducing some variations in the experimental procedures and minor modifications of the adhesives in order to attempt improvements in the physical characteristics and long term stability of capsular products.

The encapsulation trials carried out with anaerobic systems and epoxy resins are presented separately and the results obtained are also discussed in the following paragraphs.

1 - Encapsulation of anaerobic systems.

As explained in the previous Report, for the experimental work of microencapsulation of anaerobic adhesives, two representative commercial products were chosen: Loctite 270 and Loctite 290. The first product is a high strength threadlocking and medium strength retaining. The second one is a penetrating adhesive capable of locking pre-assembled parts due to its very low viscosity, usable also as sealant for porous castings and welds. Loctite 270 is a Type I, grade K, locking compound according with MIL-S-46163. Loctite 290 can be classified as a Type III, grade R, wicking compound, following the same specification. These adhesives were selected because they are widely used in industrial applications and their low viscosity (500 cP for Loctite 270 and 10-15 cP for Loctite 290) make them suitable for microencapsulation purposes.

Both systems are based on dimethacrylate esters compositions which are substantially insolubles in water. This fact allows the utilization of water as dispersing medium in microencapsulation trials.

Schematically the process used in this stage was as follows: A portion of anaerobic composition is poured into water and distributed in small discrete droplets through the aqueous medium by means of agitation with a mechanical stirrer equipped with perforated mixer blades. While continuing the agitation, the polymerization catalyst is added to the suspension, to promote the formation of the encapsulating shell. After few minutes a homopolymer shell wall has been formed around each discrete droplet and, after neutralizing the catalyst if necessary, the capsules are removed by draining through cheescloth filter. The encapsulated product remains on the filter and after washed repeatedly with water is finally allowed to dry.

As in former experiences, a number of encapsulation trials were conducted by using two catalyst systems, the first one was sodium bisulphite, the second one was a two-component redox system based on ferric nitrate and ascorbic acid. In order to investigate the effect of the process parameters on the characteristics of the capsules obtained, over twenty runs were carried out with controlled changes in the operating conditions, namely temperature of the reaction medium, addition of emulsifying agents, amount of catalyst, hardening time and agitation rate.

The major objective for those trials was the achievement of capsules with higher active core contents but maintaining proper handling and stability characteristics. A reasonable approach to reach that objective could be by reducing the observed phenomenon of premature rupture of the capsules before a shell with enough strength is achieved. This premature rupture promotes incomplete or partial filling of the primary capsules and the formation of smaller secondary capsules with the expelled liquid of the former capsules. The final effect is a reduction in the active content of the resulting capsules.

One attempt to diminish the premature rupture of capsules it was by reducing the shear forces during the agitation step. This was accomplished by using a mechanical stirrer equipped with perforated mixer blades specifically designed to provide an even dispersing action throughout the liquid medium with relatively low rotation speeds (below 300 rpm).

In order to produce capsules with appropriate sizes range, the agitation might be vigorous during the first stage of droplets formation and distribution and once completed this stage, when the hardening catalyst is added, is convenable let down the agitation speed to a level just enough to avoid the clustering of droplets during the shell's buildup phase. With the stirrer used,rotation speeds of 500-600 rpm for the first step and 200-250 rpm for the second one were found suitables to produce capsules runs with average size ranges from 300 to 600 microns.

It was realized that Loctite 290 was encapsulated more readily than Loctite 270 with the described experimental conditions. In fact because the very low viscosity of Loctite 290 (10-15 cP at 25ºC), there is not need of using any emulsifier for forming and maintaining the discrete droplets of adhesive thoroughly distributed during the hardening process, even with low stirrer speeds (200 rpm). On the contrary, when dealing with Loctite 270, due to its higher viscosity (500 cP at 25ºC) it was found convenable to use an emulsifying agent for stabilizing the droplets dispersions since without emulsifier clustering arose, particularly at lower stirrer speeds, and noticeable amounts of adhesive remaind sticked to the container walls and also to the stirrer blades. In order to avoid this trouble and to assist in the formation and distribution of discrete droplets of Loctite 270, polyvinylalcohol (PVA) was used as emulsifier in a range from about 0.5% to 1% by weight of the reaction medium.

In Table I are summarized the experimental parameters and capsules characteristics of four typical runs. These four groups of capsules were taken as basis to conduct on them the foresaid studies of this program.

It must be noticed that when no particular descriptions are given in this Report concerning with the experimental methods used for determining the adhesives or capsules properties, it is to be understood that the same instrumentation and procedures, as detailed in the previous Report (1) have been used.

In viewing the data presented in Table I, the results obtained are consistent with those of previous trials. In figures 1 and 2 are graphically presented the size distribution curves of samples encapsulated with different experimental conditions.

Figure 1 shows the capsules distribution curves of two runs carried out with Loctite 290, dispersed "in situ"

TABLE I - ENCAPSULATION TRIALS WITH ANAEROBIC SYSTEMS

	Aqueous Reaction Medium						Properties of Capsules			
ample* Code	Catalyst System Type	Conc.(%)	Emulsifier (PVAl) (%)	Temperature (ºC)	Hardening Time (minutes)	Mechanical Stirring (rpm)	Size(microns) Range	Average	Active Content (%)	Wall thickness (microns)
L9-A13	$NaHSO_3$	0.5	0.75	25	4	200	100-900	450	86.9	6-7
L9-B7	Redox	(a)	0.0	4 - 20	30	200	200-800	450	89.5	6-7
L7-A14	$NaHSO_3$	1.5	1.0	35	6	300	100-1500	600	93.0	5-6
L7-B8	Redox	(b)	1.0	35	6	300	150-1400	650	82.4	7-8

(a) Redox System constitued by 0.10% Fe^{+++} (as $Fe(NO_3)_3\ 9H_2O$) + 0.8% Ascorbic Acid

(b) " " " " 0.15% Fe^{+++} " + 1.4% " "

Adhesive content in all runs is 3.1% by weight of the aqueous medium

* IDENTIFICATION CODE: D = "In situ" dispersed
L7 = Loctite 270
L9 = Loctite 290
A = Bisulphite Catalyst
B = Redox Catalyst

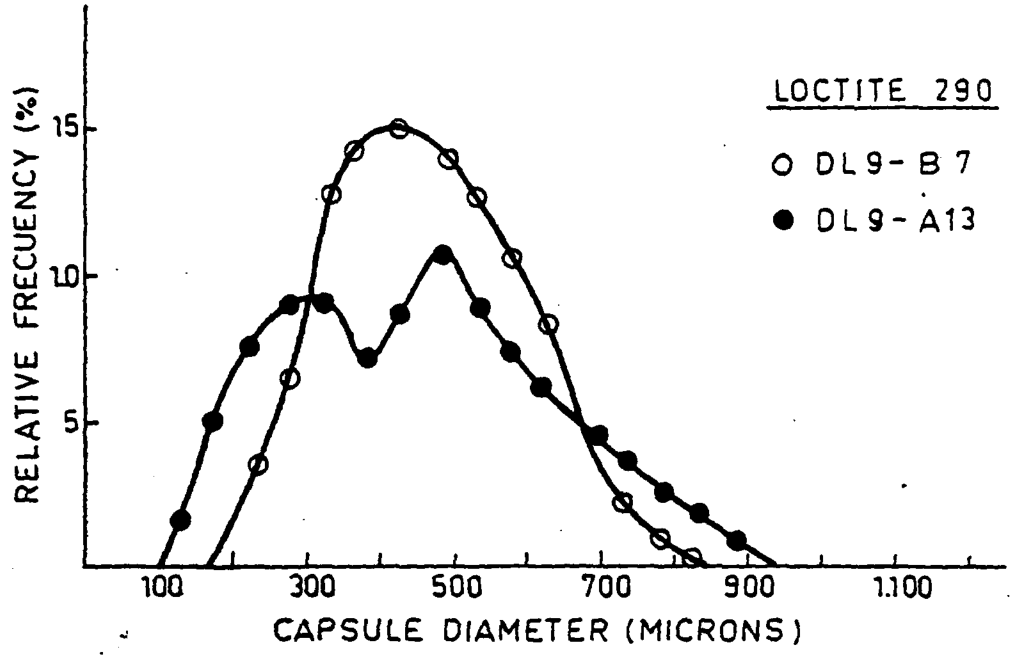

Figure 1 - Size distribution of microcapsules prepared from Loctite 290.

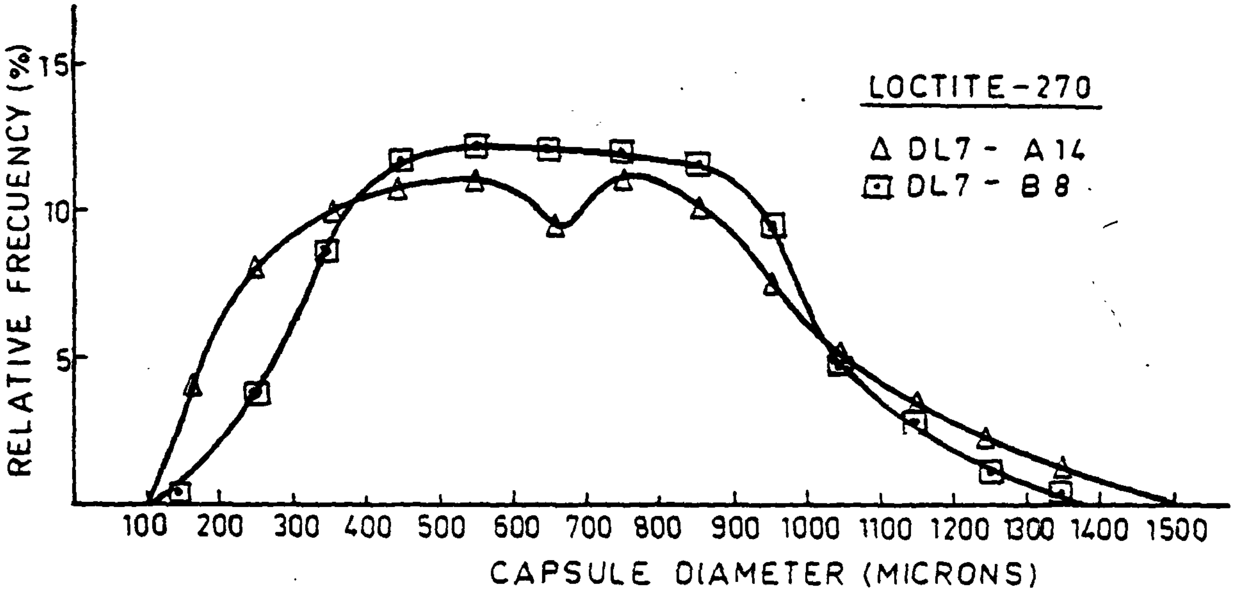

Figure 2 - Size distribution of capsules prepared from Loctite 270.

at low stirring speed (200 rpm) but using different catalyst systems and hardening schedules. The curve corresponding to the run DL9-A 13, in which sodium bisulphite was used as catalyst, shows still the double peak shape related with a premature rupture of the primary capsules. This phenomenon was however less pronounced in the present runs in comparison with the previous ones carried out with the same catalyst. By changing the bisulphite catalyst for a Redox system with lower hardening action, the "double peak" in the size distribution curve, it was not apparent, giving an indication for the permanence of a large amount of non ruptured primary capsules.

Similar results were achieved with Loctite 270, as shown in Figure 2, although some minor differences are ostensible. Thus, broader distribution curves are generated when dealing with Loctite 270 in comparison with Loctite 290, giving as result more flattish distributions and larger averages in capsules size.

A common phenomenon observed during the encapsulation processes of both Loctite 270 and Loctite 290 it was the formation of some milky haze in the dispersing medium upon addition of catalyst at the hardening stage. This haze it was noticeable in some trials, particularly with Loctite 290. This was believed to be caused by polymerization of some low molecular monomeric constituents, partially solubilized in the aqueous phase. The hazy liquid was discarded by straining and the capsules were washed repeteadly with water to remove the residual traces from their surface.

The formation of haze was practically avoided by accomplishing the dispersion step at lower temperatures (approx. 5ºC) in order to diminish the Loctite's solubility and, once completed the addition of catalyst, the temperature of the reaction medium it was raised up to 20ºC in order to shorten the timing for the hardening stage.

The modifications introduced in the operating conditions and particularly the stirring method, gave also advantageous results for the desired goal to produce capsules with higher active contents. Thus in the latest runs, capsules with core contents ranging from 82.4 to 93.0 per cent were achieved, representing a significative enhancement in comparison with the former trials in which capsules with active contents varying from 72 to 88 per cent were obtained.

Because the capsules wall thickness were very similar for both, the new runs and the previous ones, it can be assumed that the higher core contents in the capsules of the latest trials are due mainly to a better filling, facilitated by a lower degree of premature rupture in the capsules formation step.

The durability and handling properties of the new sets of capsules were found to be equivalent to the former runs.

In figures 3 and 4 are shown photographies of typical capsules produced in these runs.

2 - Encapsulation of epoxy resins.

The microencapsulation trials with epoxy resins conducted on the initial part of this program have been extended with studies on the effect of the addition of different chemicals into the epoxy system on capsules shell formation and on subsequent capsules properties. Fur-

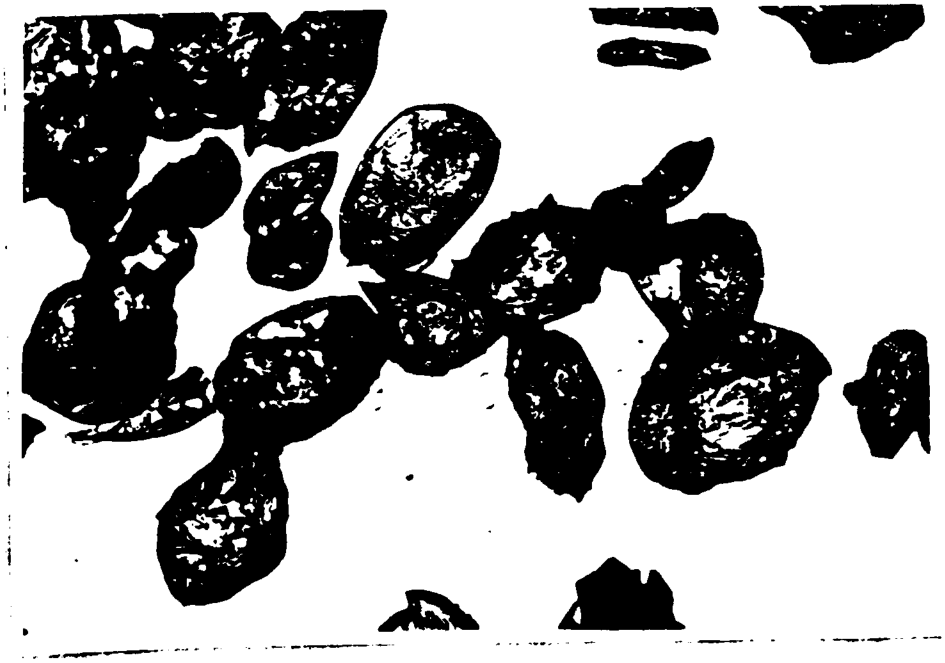

Figure 3 - Loctite 270 capsules produced with Redox catalyst. (Sample DL7-B8). Magnification 28 X.

Figure 4 - Loctite 290 capsules produced with sodium bisulphite catalyst. (Sample DL9-A13). Magnification 24 X.

therwise, some additional trials were carried out with different operating conditions, e.g. at temperature above the ambient, at different sprayhead speeds, and with different hardening time.

In order to get comparable results in relation with the previous trials, the same raw materials and experimental procedures were used in the actual stage. Thus these trials were conducted on the same epoxy resin: BEPOX LX/21, from GAIRESA.

As explained in the previous Report and accordingly with the results of the chromatographic analysis presented in Part E of this Report, Bepox LX/21 is a low viscosity, liquid epoxy resin based on dyglycidyl ether of bisphenol A (DGEBA) which contains aprox. 22% pbw of cresyl glycidyl ether as reactive diluent.

For encapsulation purposes, the centrifugal technique was used, as before, with the same centrifugal sprayhead and similar operating conditions, e.g. a spreading height of 15 cm. and rotation speeds in the range of 1200 - 2000 rpm. As hardening bath it was used a catalyst prepared by adding 20% of water (V/V) to BF_3 etherate and subsequent removal of the liberated ether by distillation in vacuum. This catalyst have been proved to give the best results in the former trials, although in some runs of the actual phase the capsules showed a pink coloring which was intensified by ageing, leading to a progressive shell buildup and capsules hardening. It is assumed that this detrimental pink coloring is caused by residual catalyst traces, because this troubles can be avoided by a careful neutralizing action of those catalyst traces by washing with sodium carbonate and then washing repeatedly with water until neutral pH is reached.

In Table II are summarized the experimental parameters of a representative list of encapsulation runs and typical properties of the capsules produced.

In general, the results of these complementary trials are in good agreement with those of the initial phase, and some significative observations are presented in the following paragraphs.

a) Effect of resin temperature.

At 20ºC Bepox LX/21 has a viscosity of around 2000 cP. This forces high rotation speed to the sprayhead to produce acceptable droplets of about 400 to 600 microns of average size. Conditioning the resin at 40ºC before the spraying step reduces its viscosity to 250 cP, allowing thus the use of substantially lower rotation speeds to obtain capsules of similar sizes or even smaller than those obtained with the resin maintained at room temperature (20ºC). On the other hand this low viscosity allows narrower capsules size distribution.

In viewing of the Table II it can be seen, by comparing the data of samples EB 2-2 and EB 2-4 (encapsulated at 20ºC) in relation with EB 4-1 and EB 4-2 (encapsulated at 40ºC with the same sprayhead rotation speeds), that both the size distributions and average capsules size have been reduced to less than a half in all cases.

In Figure 5 are graphically presented the size dis-

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TABLE II - ENCAPSULATION TRIALS WITH BEPOX LX/21

Sample Code	Catalyst System	Hardening Time (Hours)	Resin Additive (Parts/100)	Resin Temperature (%)	Sprayhead Speed(rpm)	Size Range	Microns Mean	Active Content (%)	Wall thickness Avg.(mic.)
EB 2-2	BF_3O T_2/H_2O (100/20)	2	---	2.0	2.000	200-1000	500	70.3	9.2
EB 2-4	"	4	---	20ºC	1.300	250-1200	800	82,6	10.0
EB 4-1	"	2	---	40ºC	2.000	50-450	200	67.2	9.5
EB 4-2	"	2	---	40ºC	1.300	50-650	350	69.1	9.3
EB 6-1	"	2	α-naphtylamine (1.0)	20ºC	2.000	200-1100	570	0.0	---
EB 7-1	"	2	p-nitroaniline (0.5)	"	"	250-1150	630	74.1	8.8
EB 8-1	"	2	triethanolamine (1.0)	"	"	200-1050	580	90.6	7.0
EB 8-2	"	2	triethanolamine (0.5)	"	"	200-1000	600	88.6	7.4
EB 8-3	"	2	triethanolamine (0.1)	"	"	200-1000	500	76.9	8.3

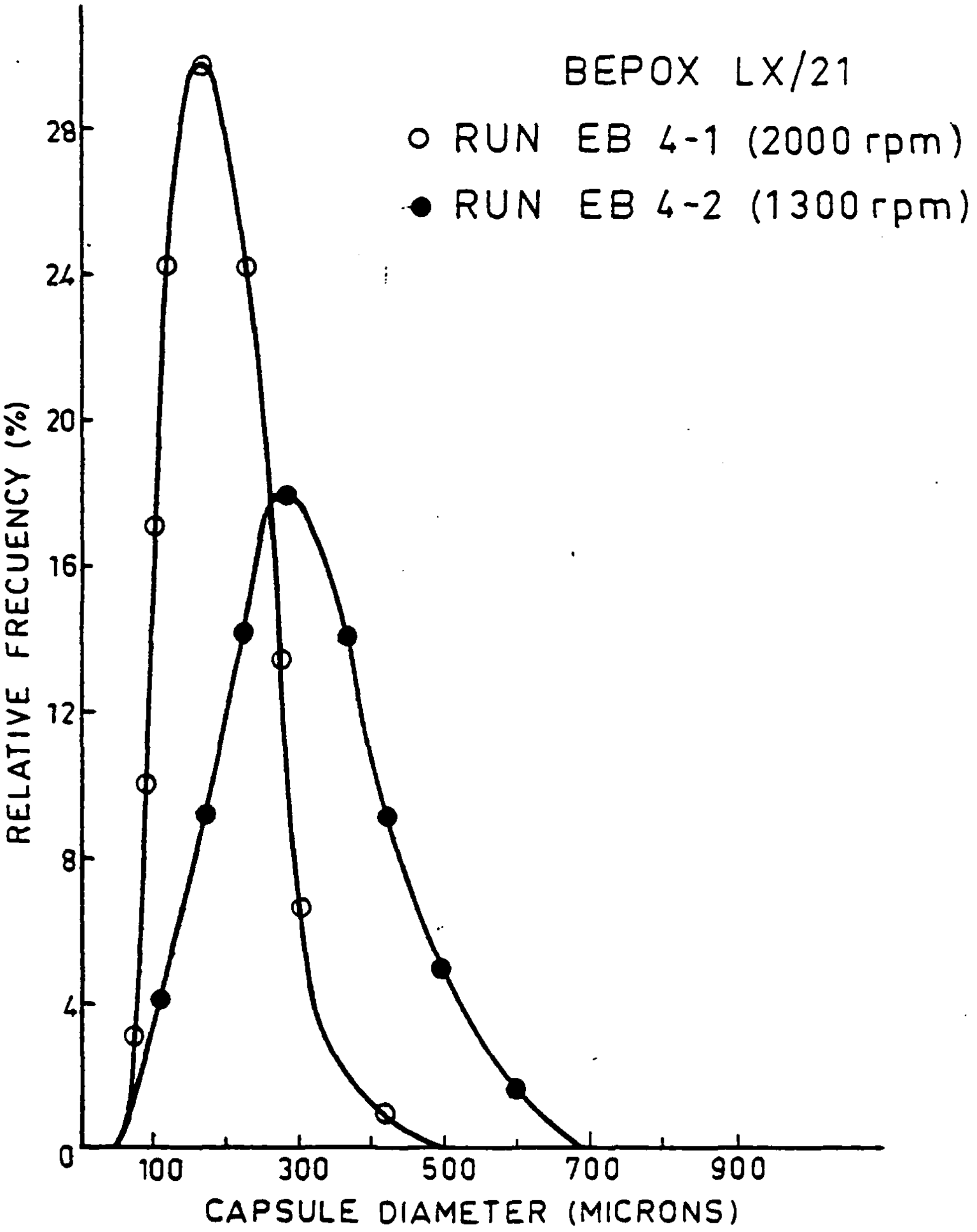

Figure 5 - Size distribution of epoxy microcapsules produced at 40ºC, with different spray-head rotational speeds.

tribution curves of two typical runs carried out at 40ºC with different sprayhead rotational speeds. Both curves are gaussion type and the ones corresponding to the run of higher rotational speed shows smaller capsule sizes and narrower distribution range.

b) Effect of sprayhead rotation speed.

As it was expected, when using lower rotation speeds, capsules with greater average size were produced. Although it is noticeable that this increase in the average size is not correlated with an equivalent enlargement of capsules size distribution, at least in the range of angular velocities used in these tests (1300 and 2000 rpm.).

c) Effect of hardening time.

By comparing the data of EB 2-2 and EB 2-4 samples in which hardening times of 2 and 4 hours were consumed, only a slight influence is appraisable, corresponding to a small increase in shell thickness (10.0 μ versus 9.2 μ). This relatively small difference indicates that after 2 hours of stay in the hardening bath, the rate of shell buildup is very low and in consequence, it can be assumed that an inmersion time of 2 hours is sufficient to attain durable capsules.

d) Effect of resin additives.

The presence of additives in the resin to be encapsulated can affect markedly to capsule wall formation and to subsequent capsule properties.

In order to asses the influence of resin additives, encapsulation trials were conducted in which minor amounts (up to 1%) of α-naphtylamine, p-nitroaniline and triethanolamine, were alternatively added to the Bepox LX/21 resin.

The following results were obtained:

α-naphtylamine: Amounts varying from 0.2 up to 1.0 per cent were added to Bepox LX/21 and then encapsulation trials were carried out using the same procedures as previously described.

The capsules obtained were softer then the ones without additives. Nevertheless, these rubber like capsules showed a progressive hardening that couldn't be avoided with a careful neutralization and repeatedly washing with water.

p-nitroaniline: This chemical was used as additive because according to Flynn (2) retards the rate of shell formation inhibiting further shell buildup to a considerable extent.

p-nitroaniline was used with a ratio 0.5 to 100 parts of resin. After thoroughly mixing, the resulting mixture showed an orangy color and when encapsulated the capsules showed a darker color and brittle but durable shell characteristics.

Hardening time schedules varying from 1 to 6 hours were used. The active contents, determined by solvent extractions, decreased inversely to the length of inmersion in the catalyst bath, in the same way

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(2) E.J. Flynn and D.E. Eaves - Adhesives Age, 20, 3, 37-42 (1977).

as happens to the resin without additives.

These capsules shown a slight tendency to a progressive shell buildup, diminishing its active contents under long term storage conditions, as can be seen in Figure 10 of Part C (pag. 33), in which are graphically represented the variations in active contents versus time of epoxy capsules with and without additives. The capsules containing p-nitroaniline correspond to the sample coded as EB-7-1.

Triethanolamine: This chemical was also used as additive for Bepox resin in encapsulation trials. Ratios varying from 0.1 up to 1.0 parts per cent were used and hardening schedules from 1 hour to 6 hours were also used.

Capsules with high active contents, up to 90.6% were obtained, as can be seen in Table II, and these capsules shown really good long term stability as can be viewed in Figure 10 above mentioned.

In figures 6 and 7 are shown photographies of typical capsules produced in these runs.

Figure 6 - Epoxy capsules produced in run EB 2-4 at 1300 rpm and 20ºC. Magnification 38 X.

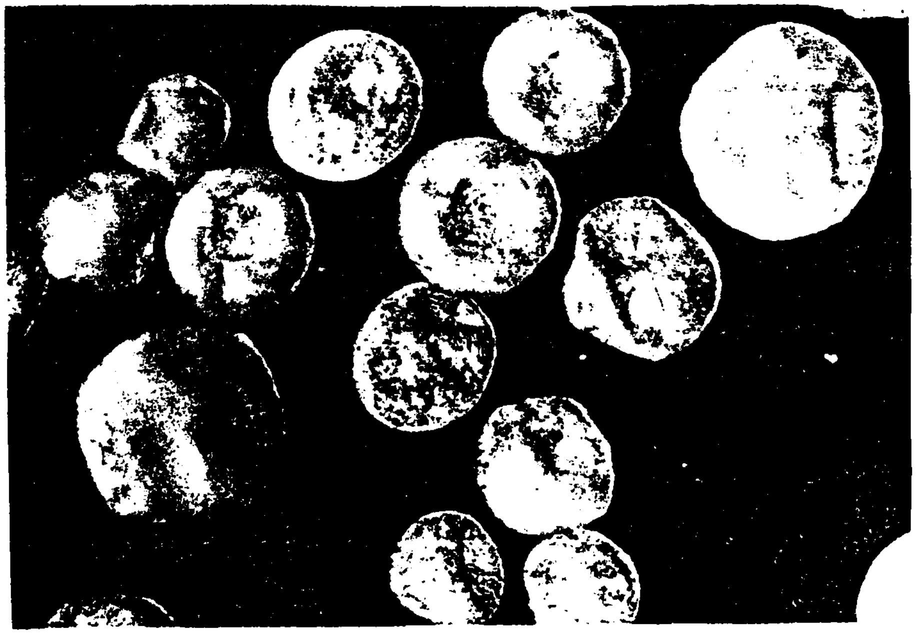

Figure 7 - Epoxy capsules produced in run EB 8-2, at 2000 rpm, 20ºC, and 0.5% trietanolamine. Magnification 38 X.

B - Preparation of capsules epoxy adhesives with improved homogeneity.

During the initial phase of this program, several attempts to prepare capsular adhesive systems were conducted. The first attempts dealt with the preparation of "paste" adhesive curable at room temperature, by mixing in the proper ratio the epoxy capsules with a liquid hardener. These attempts were unsuccesful because after few days, the amine based curing agent penetrated through the shell causing the premature hardening of capsules.

Durable heat curable capsules adhesive systems were developed with a physical form of dry free flowing granulate by mixing epoxy capsules with a finely divided solid hardener such as methylenedianiline (MDA). Formulations with Bepox capsules/MDA ratios from 100/19 to 100/22 w/w gave the best bonding strengths.

However some erratic results were obtained in the adhesion tests which are presumably caused by non homogeneous mixing or settling effects.

In order to enhance the homogeneity and long term stability of capsular formulations, some attempts were conducted in which the individual capsules containing the epoxy resin are coated with discrete portions of solid curing agent anchored on the capsules surface.

The approach to achieve this physical anchorage consisted in disolving the solid hardener in a suitable solvent which is non solvent for capsule's shell neither affects to its contents. Once prepared the hardener solution, the appropriate ratio of capsules is added and distributed into the solution. Then, by progressive evaporation of the solvent a phase separation of hardener is produced. Upon completion of solvent evaporation, a substantial portion of the solid hardener is anchored on the outside surface of the discrete resin capsules giving dry, free flowing capsular adhesive, with the required hardener's content and homogeneously distributed.

In the first phase of this program a number of trials were conducted with different solvents. Further tests were carried out with three solvents: "butylcellosolve", dioxane and isopropanol. These solvents were chosen because their little, if any, solvent action on epoxy capsules and, on contrary, their fair solvent power on MDA hardener used (HT 972, from CIBA GEIGY).

The three solvents above mentioned proved to be capable of depositing the MDA proportions required for a proper cure (between 19 and 22 parts per cent of resin). However, in spite of the initial promising results none of them gave satisfactory long term results.

Butylcellosolve presents the problem of its low volatility offering difficulties in its removal by evaporation. The residual solvent leads to formulations rather paste like instead of dry, free flowing systems, and, in addition, such formulations are showed a lack of stability, leading to a progressive hardening.

When dealing with dioxane it proved to be not so good solvent for MDA as butylcellosolve but, on contrary, it can be removed relatively easy by evaporation providing dry, free flowing capsular systems. However, it was observed that the shell of epoxy capsules is relatively permeable to dioxane. This permeability allows the penetration through the shell of some amounts of MDA hardener dissolved in causing further polymerization of the capsule's contents resulting finally in a considerable hardening of the capsules.

Better results were reached with isopropanol which is a poor solvent for MDA at room temperature but increases considerably its solvent action when the temperature is raised up to 50 - 60ºC. However, the problem of penetration of dissolved hardener through capsule's shell subsisted, although less markedly than with dioxane.

In general, the aliphatic alcohols with longer chains such as n-butanol or amyl alcohol, showed the best results.

Schematically, the procedure for producing hardener's coated capsules was as follows:

n-butanol is added to a predeterminate amount of MDA in a ratio 1/1 w/w. To facilitate the disolution of MDA gentle warming up to 50ºC is required. Once the mixture has been completed, a liquid paste is formed to which the epoxy capsules are added in adequate quantity and thoroughly mixed in order to achieve an homogeneous mixture in which the capsules are individually coated with a continuous wet film of MDA. The final step is a drying process in which n-butanol is forced to evaporate, converting the "wet" MDA film in a solid coat anchored to the capsules surface.

This drying step was carried out by using the fluidized bed technique, with air flow as suspension and drying medium.

Once completed the process, an even dry, free flowing granulate was obtained with a deep yellow color.

The granulates produced as previously described are very stable on handling, because do not have problems of hardener's separation by settling.

C - Capsular adhesives stability.

In the initial planning of this Project it was outlined, as a major goal, the assessment of stability for the capsular systems to be developed in the course of the research.

Therefore, studies for determining long term capsules stability have been conducted on both, anaerobic and epoxy capsular systems, in order to know the permanence of its original properties and functionality, not only as isolated or single encapsulated products, but also the stability of the whole system when mixed with other active ingredients, such as curing agents, to form formulated adhesive systems.

Within this objective, samples of the capsular systems have been subjected to ambient aging tests for periods ranging from few days up to 18 months, depending on the severity of aging conditions.

The capsular samples were stored in different ambient environments where temperatures ranged from 20ºC to 40ºC and relative humidity varied from 35% to 85%. Other samples were artificially aged upon exposure to ultraviolet radiations from fluorescent lamps, and other aliquots were stored in closed vials, in dark cabinets, for comparative purposes.

During the program, periodical examinations were performed to determine variations in physical characteristics of capsules and the limits for functionality of the adhesive systems.

These periodical examinations were focused in determination of core contents variations, chemical modifications in capsules core, and, finally, variations in bonding properties of aged capsular adhesives.

For determining the capsules core contents, the method of quantitative extractions with chloroform was used, as described in the previous Report. This method is suitable for both, anaerobic and epoxy encapsulated systems. For Loctite capsules the extraction processes were carried out at room temperature in order to avoid further polymerization of the encapsulated material caused by heating. For epoxy capsules, hot extraction in soxhlet were preferred.

For the assessment of chemical modifications in capsules contents caused by aging processes, liquid chromatographic analysis have been performed. This analysis will be discussed later, in Part E, concerning chemical characterization.

Similarly, adhesion studies on aged capsular adhesives will be discussed separately in Part D of this Report.

In the following paragraphs are presented the results related with core contents variations in both, anaerobic and epoxy capsular systems.

1 - Stability of capsular anaerobic systems.

Samples of several batches of encapsulated anaerobic adhesives have been subjected to ambient aging tests in four different environmental conditions:

a) Standard atmosphere, 23ºC ± 2ºC and 50%±5% HR
b) at 40ºC ± 2ºC and 85% ± 5% H.R.
c) at 40ºC ± 2ºC and 35% ± 5% H.R.
d) Under ultraviolet light at 40ºC ± 2ºC

In figures 8 and 9 are presented graphically the results of periodical evaluations of core contents in relation with storage conditions at different temperatures and humidity levels.

Figure 8 shows the effect of environmental conditions on encapsulated Loctite 270. In viewing this figure can be seen that the capsules of this product exhibit a satisfactory stability when stored in standard atmosphere of 23ºC and 50% H.R., because a storage period of 8 months a decreasing of less than 6% in core contentsis observed. Even after one year of storage, a core contents of 76% is maintained, with decrease of 17% referring to the original contents.

The same figure shows clearly the detrimental effect of storage at temperatures above the ambient, for both, high or low humidity levels. From the point of view of core contents shortage, the limits for capsular shelf life at 40ºC can be fixed for Loctite 270, between 4 and 6 months. When the capsules are stored in high humidity environments a gain of weight is observed in the initial period of exposure (up to 2 or 3 months). It is assumed that under these ambient conditions the capsules absorb moisture and swell, thereby increasing the weight of the extractable fraction which is evaluated as core contents.

In figure 9 are presented the effects of environmental conditions on encapsulated Loctite 290. The graphics of this figure are consistent with those in figure 8, and, therefore, encapsulated Loctite 290 exhibit, in general, similar stability characteristics as Loctite 270.

Encapsulated samples of Loctite 270 and Loctite 290 were exposed to ultraviolet light in an accelerated aging chamber provided with fluorescent lamps. The emitting UV

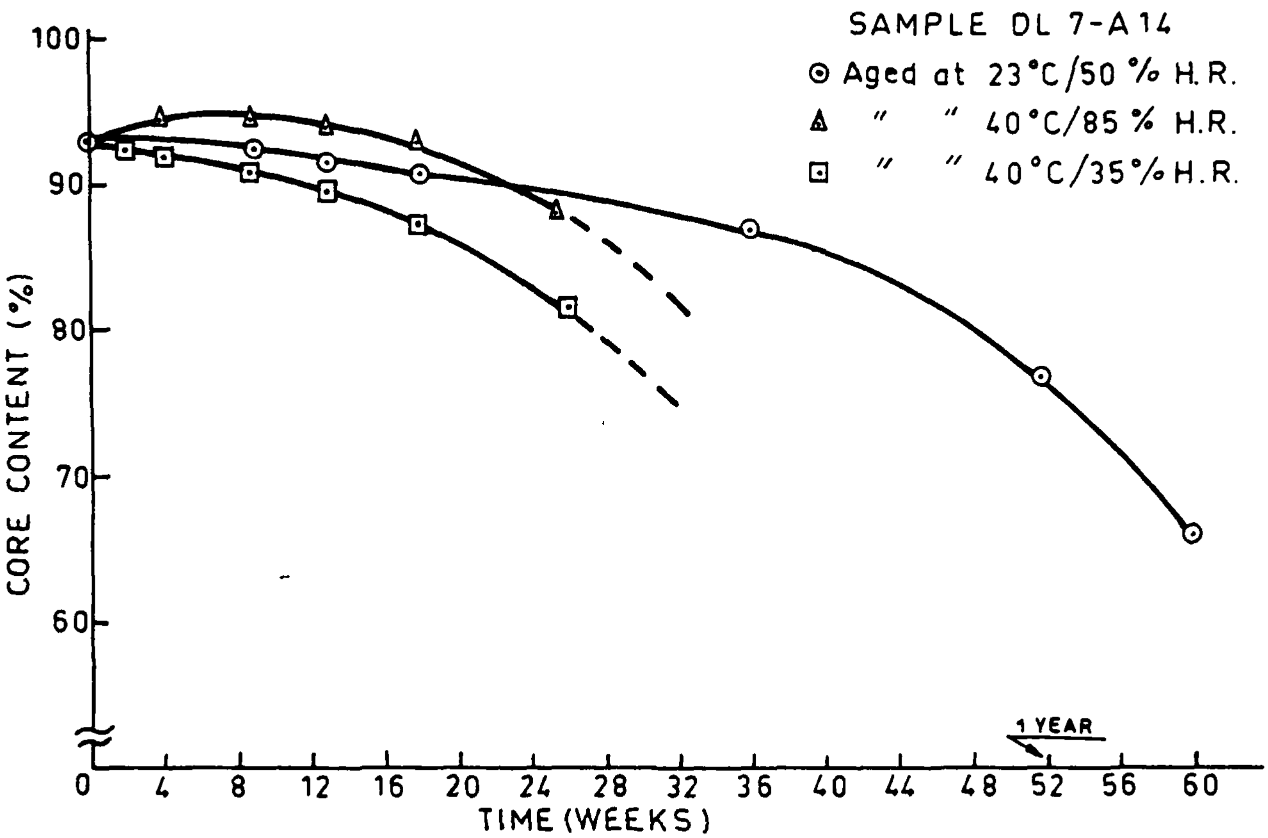

Figure 8 - Stability of encapsulated Loctite 270 stored in different ambient conditions.

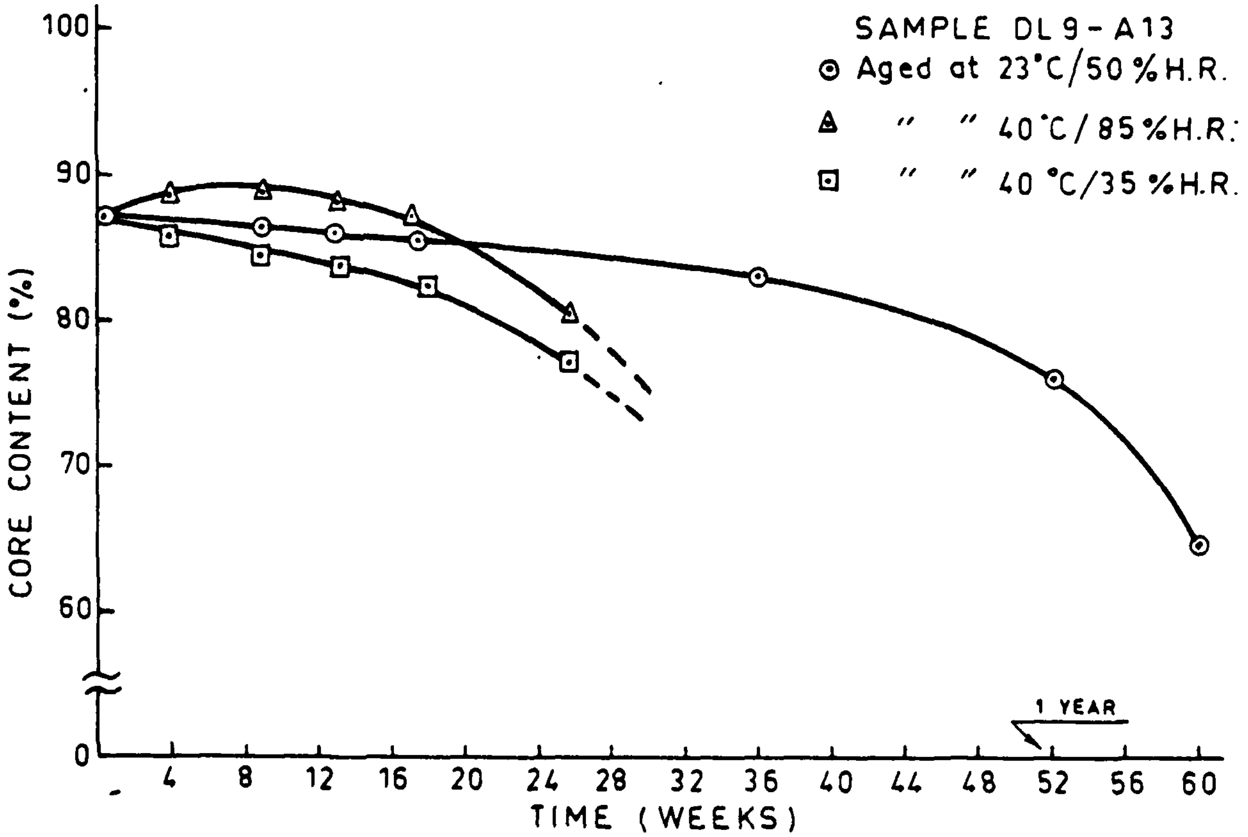

Figure 9 - Stability of encapsulated Loctite 290 stored in different ambient conditions.

spectrum of these lamps is in accordance with specification ASTM G-53. During operation, the samples were maintained at 40ºC ± 2ºC and were exposed at UV energy level of 1.6 W in the range of 280-350 nm. Each sample was divided into three aliquots which were exposed for 24, 48 and 72 hours respectively.

The results of these tests indicate that Loctite 290 capsules are more sensitive to UV radiations than Loctite 270 does. The first ones are discoloured rapidly and harden, diminishing its active contents substantially in short time (less than 48 hours of exposure).

In case of Loctite 270 capsules, there is a slower process of decoloration, changing from the blue color to green and then to yellow shade. The active contents of these UV exposed Loctite 270 capsules decreases also substantially, but at lower rates than the Loctite 290 ones.

A side effect for both Loctite's capsules is the stiffening of the shell, that becomes much harder than the original skin upon UV exposition.

2 - Stability of capsular epoxy systems.

A number of tests for determining the effect of environmental conditions on storage stability of encapsulated epoxy systems have been carried out.

These ambient aging tests were conducted on epoxy capsules as single constituent, and on the whole capsular adhesive systems, e.g. encapsulated resins plus curing agents.

Variations in active contents were used as primary parameter for evaluating the capsules aging process.

Periodical measurements of capsules core contents were performed by chloroform extractions, as previously described, and the chloroform soluble fraction was accepted as active contents.

In figure 10 are presented graphically the long term stability (up to 18 months) for different runs of Bepox capsules stored in standard ambient conditions: 23±2ºC, 50±5% HR

It can be seen that Bepox LX/21 capsules obtained from neat resin, without additives (samples EB 2-2 and EB 2-4), remain stable as for its active contents even 75 weeks (18 months) after their formation, which indicates an excellent stability under the mentioned conditions.

In the same way, Bepox capsules containing 0'5 parts per cent of triethanolamine as additive (sample EB 8-2), show similar stability to the above mentioned capsules.

Capsules containing 0'5 parts per cent of p-nitroaniline (sample EB 7-1) show, however, certain tendency to progre-

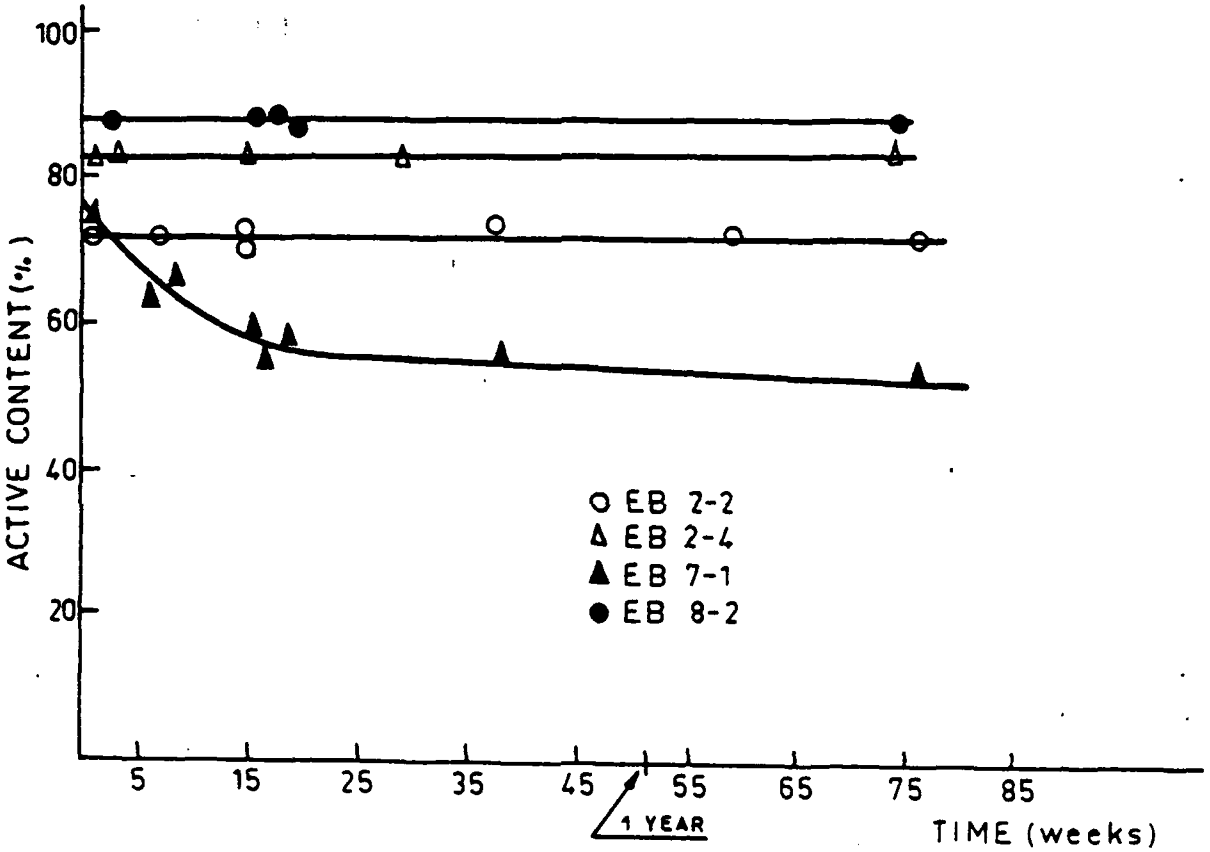

Figure 10.- Long term stability of encapsulated epoxy resin, with and without additives.

ssive hardening. This tendency is sharper at the beginning and after aprox. 6 months stabilizes with a slight negative slope. Comparatively these capsules have an active contents 20 to 30 percent lower than the other capsules.

Furthermore, some samples of Bepox capsules were exposed to ultraviolet light, in the same apparatus and similar test conditions, than used with anaerobic (Loctite) capsules. The primary effect that can be observed on the capsules is a darkening of the shell, as well as an increase of the shell's stiffeness. Moreover there is a moisture loss that is partially reflected in the reduction of chloroform extract in the first two days of exposure, as can be seen in Figure 11, that shows the core contents variation in a sample of encapsulated Bepox, subjected to UV radiations for up to 20 days.

Dry formulations of the Bepox capsules with hardener HT 972 stored at 23ºC and relative humidity ranging between 50% and 70% do not change significatively its active contents.

However, for high relative humidity these formulations tend to become lumpy forming a mixture with no free flowing properties. This, nevertheless do not affect the adhesion properties (as proven further on in Part D). Formulations obtained by deposit of MDA on the capsular shell by the previously described process of disolving the hardener in n-butanol followed by fast evaporations of the same, when stored at 23ºC and R.H. = 50% show a tendency to progressive hardening, possibly due to the penetration of the hardener through the capsular shell in the application process.

D - Adhesion studies.

The adhesion studies initiated in the first phase of this Project have been continued during the program extension covered by this Report.

The initial scope for these tests dealt with the assesment of bonding properties of the adhesive compositions related with the Project, either in their liquid original state or in capsular form, providing a data basis for evaluating the improvements or shortages introduced in the adhesive by the microencapsulation processes.

In the course of this Project additional adhesion tests have been carried out on samples of capsular systems previously aged in different environmental conditions during different time lapses The purpose of these tests is to get complementary data about capsules stability throug the permanence of bonding properties in capsular systems after aging processes.

These tests have been conducted by using the same method as in former studies. Lap shear in accordance with ASTM A-1002, because its simplicity to prepare and test a large number of specimens with statistical significance and, therefore, its wide acceptance for comparative adhesives test. Lap shear tests were carried out in a TTCM: Instron machine. In all cases the load was applied at a constant crosshead speed of 1.0 mm/min. The specimens were conditioned and tested at 23ºC, 50 ± 5% RH.

The only changes introduced with regard to the previous tests concerns the substrate used in these adhesion tests Mild steel used formerly was replaced by aluminum alloy 2014-T6. Strips of 120 x 252 x 3 mm were used in lap shear tests. The 3 mm thickness of these strips proved suitable to prevent flexural plastic deformation of spe-

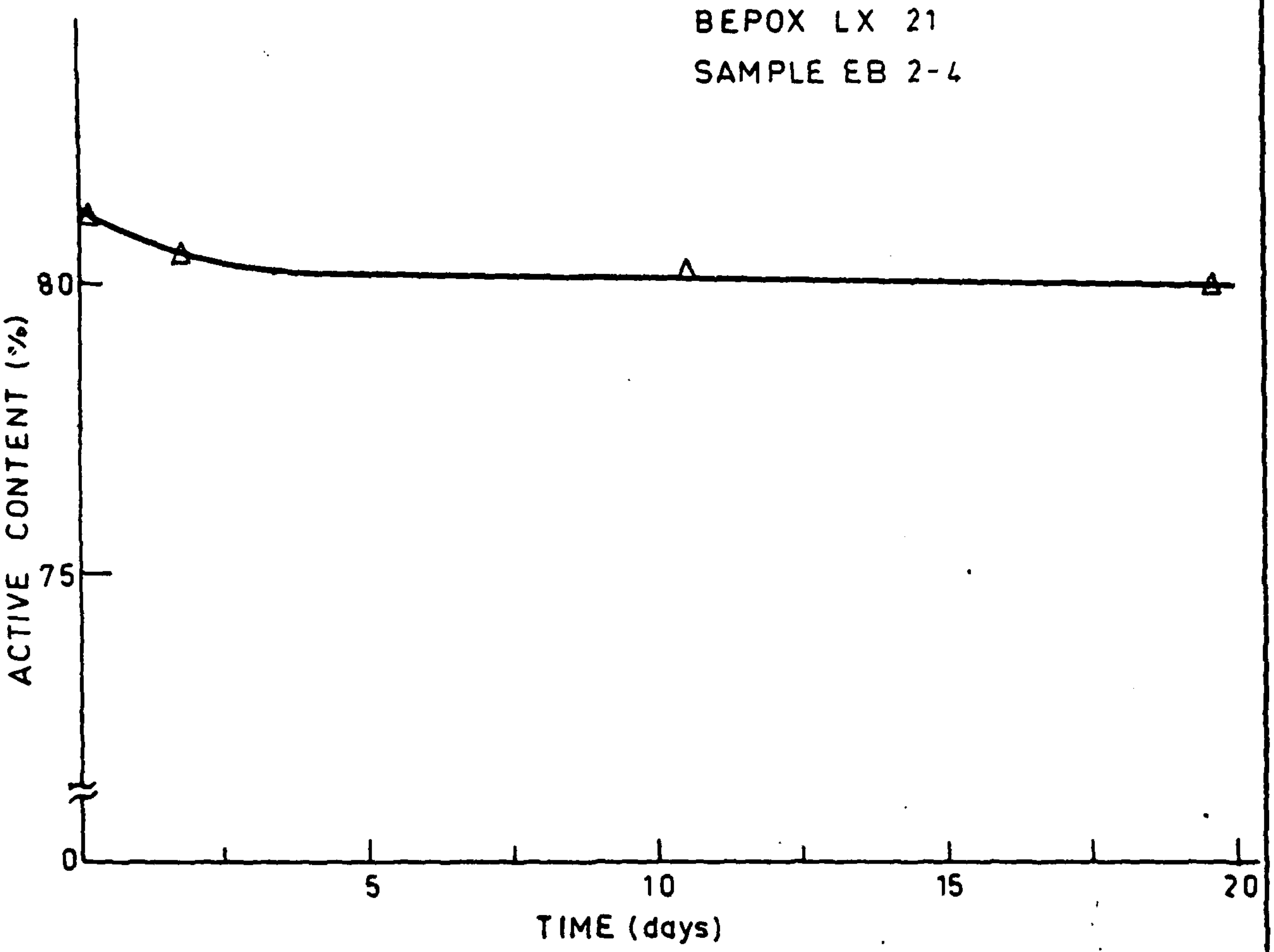

Figure 11 - Stability of epoxy capsules exposed to ultraviolet light.

cimens during lap shear tests.

The following method was used for adherent's surface preparation, before bonding:

1 - Degreasing with trichloroethylene
2 - Etching during 20 minutes at 60ºC ± 2ºC in the following solution:

96% sulfuric acid	275 pbw
sodium dichromate...............	75 "
demineralized water	850 "

3 - Wire brushing
4 - Rinsing with distilled water
5 - Oven drying below 60ºC

In the following paragraphs are discussed separately the adhesion studies conducted on both, anaerobic and apoxy systems.

1 - <u>Adhesion tests on anaerobic systems.</u>

The results obtained in the comparative lap shear tests conducted on both, unencapsulated and encapsulated anaerobic adhesives, during the initial phase of this Project showed, as presented in the previous Report, an apparently anomalous behaviour because in several runs the adhesive strengths of lap shear specimens bonded with encapsulated systems were higher than those achieved with the original, unencapsulated systems.

In order to confirm or modify these initial results, further adhesion tests have been conducted in which an aluminum alloy has been used as adherend substrate instead of mild steel, as previously indicated. These tests have been carried out with closer control of specimens surface treatment, bonding procedures and experimental method in lap shear tests. The results of these tests are presented below.

a - <u>Lap shear tests on unencapsulated anaerobic adhesives.</u>

In Table III are presented the tests carried out on both Loctite 270 and Loctite 290 in their original liquid form.

Different hardening schedules have been used, following the guide-lines of previous tests. The results confirm the fact that, in order to reach fully bonding properties, it is necessary to accomplish the hardening process at temperatures above the ambient. A hardening schedule of 48 hours at 75ºC ± 5ºC gave satisfactory results and was chosen as standard schedule for forthgoing adhesion tests.

In these conditions, lap shear values of aprox. 13 MPa were attained with Loctite 270, that are practically 100% higher than those achieved on mild steel in the former tests. In the case of Loctite 290 the differences are not so acute, but are still noticeable 9.6 MPa vs. 7.9 MPa, e.g. approx. 20% over.

b - <u>Lap shear tests on encapsulated anaerobic adhesives.</u>

In Table IV are summarized the results obtained in lap shear tests with encapsulated Loctite 270 and Loctite 290. All tests were carried out with the standard hardening schedule of 48hr/75ºC., and the same experimental procedure as in former tests for capsules spreading and rupturing. In order to achieve controlled bond thickness, adequate spacers(gauge films) were used.

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TABLE III - LAP SHEAR ON UNENCAPSULATED ANAEROBIC ADHESIVES

Sample Code	Adhesive System	Hardening Schedule	Surface Preparation	Specimens Number	Shear strength Mean values ($\bar{x}$) (MPa)	Standard Deviation (σ)	$\sigma/\bar{x}$
$L70-N_6$	Loctite 270	24h. at 22ºC	Sulfochromic etching	6	6.21	0.89	0.143
$L70-N_7$	"	4h. at 60ºC	"	6	10.0	1.09	0.110
$L70-N_8$	"	24h. at 20ºC + 24h. at 75ºC	"	9	11.5	1.38	0.12
$L70-N_9$	"	48h. at 75ºC	"	6	13.1	1.09	0.083
$L70-N_{10}$	"	72h. at 75ºC	"	6	13.0	3.75	0.288
$L70-N_{11}$	"	144h. at 75ºC	"	6	14.6	3.41	0.233
$L90-N_4$	Loctite 290	24h. at 75ºC	"	6	9.04	0.39	0.044
$L90-N_5$	"	72h. at 75ºC	"	8	9.64	0.49	0.051
$L90-N_6$	"	144h. at 75ºC	"	6	9.90	0.49	0.049

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TABLE IV - LAP SHEAR ON ENCAPSULATED ANAEROBIC ADHESIVES

Sample Code	Adhesive System	Hardening Schedule	Surface Preparation	Specimens Number	Adhesive Bond Thickness (microns)	Shear Strength Mean Values ($\bar{x}$) (MPa)	Standard Deviation (σ)	$\sigma/\bar{x}$
DL7-A12	Loctite 270	48h at 75ºC	Sulfo-chromic etching	10	50	7.85	0.73	0.09
DL7-A14	" "	" "	"	10	50	7.98	0.57	0.07
DL7-B8	" "	" "	"	10	50	9.91	0.62	0.06
DL9-B5	Loctite 290	48h at 75ºC	"	10	50	7.65	0.89	0.11
DL9-B6	" "	" "	"	10	100	7.70	1.03	0.13
DL9-B7	" "	" "	"	14	50	6.89	1.28	0.18

In comparing the values of this Table, it can be seen that the figures obtained with Loctite 270 are fairly higher than when Loctite 290 is being used. However when relative values are considered, taking as basis the original unencapsulated lap shear strengths for each Loctite system, the results of these evaluations are changing, because the permanence of bonding properties is slightly higher for capsular Loctite 290 (80% with regard to the lap shear on the original liquid form), than for Loctite 270 (76% of bonding permanence).

Finally a comparison of these values with regard to those obtained in previous tests, doesn't confirm the initial results related to an apparent improvement when using encapsulated Loctite systems. On the contrary, a detrimental effect of about 20 ÷ 25% in adhesion has been observed when dealing with encapsulated systems. In consequence, it is assumed that a lack in adhesion of unencapsulated Loctite systems on mild steel was the cause that lead to the low shear strengths measured in initial tests.

C - Effect of aging on lap shear strength of encapsulated anaerobic adhesives.

Two runs of encapsulated Loctite 270 and Loctite 290 were divided in aliquots and subjected to aging by storing them under different environmental conditions during different lapse of time. After the storage period, lap shear tests were conducted on specimens bonded with the aged adhesives and the resulting shear strengths were measured.

In Table V are summarized the results of these tests which shows the effect of environmental storage conditions on lap shear properties.

TABLE V - EFFECT OF AGING ON LAP SHEAR STRENGTH OF ENCAPSULATED ANAEROBIC ADHESIVES

ENVIRONMENTAL CONDITIONS

	A (23ºC/50% RH)		B (40ºC/35% RH)		C (40ºC/85% RH)	
Sample Code	Time (days)	Shear Strength (MPa, Average)	Time (days)	Shear Strength (MPa, Average)	Time (days)	Shear Strength (MPa, Average)
Loctite 290 (DL9 - B7)	2	7.10	2	7.26	2	6.84
	74	6.23	14	7.96	14	7.04
	300	5.84	28	7.85	28	7.18
			56	7.03	56	6.91
Loctite 270 (DL7 - B8)	2	9.97	2	10.3	2	11.2
	74	9.43	14	10.8	14	13.0
	300	8.02	28	11.6	28	12.3
			56	11.4	56	11.7

Curing schedule: 48 hours at 75ºC ± 5ºC in all tests.

These results indicate that when stored in standard ambient conditions (23ºC/50% RH), the shelf life extends over 10 months for both encapsulated Loctite systems. As the limiting storing life for these systems in their original liquid form is approx. one year, according with producer's instructions, it is apparent that encapsulation processes conducted on these systems do not cause detrimental effects on its storage stability.

The results obtained on other aliquots stored at 40ºC with high and low humidity levels for periods up to 2 months, indicate a general improvement in lap shear strengths of capsules stored at moderate temperature above ambient. Slight differences can be observed in the storage behaviour of Loctite 290 and Loctite 270. Whilst the first one shows a little bit higher values on dry storage, the second one present clearly better shear strenghts on moist conditions. It must be noticed anyway that these results are related with short and medium term exposure tests and can not be extrapolated to long term behaviour, because as demonstrated in other stability tests concerning active content variations, the limits for capsular shelf life at 40ºC can be fixed for both Loctite 270 and Loctite 290 in the range of 4 to 6 months. (See stability studies in Part C.1 of this Report, page 29 and 30).

2 - Adhesion tests on epoxy systems.

In order to asses the effect of microencapsulation processes on adhesive properties of epoxy systems, a number of lap shear tests were conducted on unaged and aged capsular samples. These tests were carried out by using the same aluminum substrates as explained before for anaerobic systems and with identical experimental procedures. The only differences concerns the pressure applied for rupturing the capsules: 170 MPa for epoxy capsules, and curing schedule (4 hr at 100ºC + 8 hr at 140ºC).

a. Lap shear tests on unencapsulated systems.

In order to get an adequate reference basis, lap shear tests were conducted on a set of 20 specimens bonded with unencapsulated Bepox LX/21/HT 972 system in ratio of 100/27 pbw. An average shear strength of 16.1 MPa was obtained for this sample.

This value is within the same range of those achieved in former tests with mild steel as substrate: 15'1 MPa and 15'9 MPa, depending on surface treatment.

b. Lap shear tests on encapsulated systems. Effect of aging on bonding strength.

Following the same ageing schedule as previously described for anaerobic systems, several samples of encapsulated Bepox resin were divided in aliquots and subjected to various environmental conditions for different time lapses.

In Table VI are presented the tests conducted and the results achieved.

In viewing that Table it can be seen that capsules kept in standard ambient (23ºC/50% RH) do not present noticeable ageing signals during a seven months test time,

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TABLE VI - ADHESION TESTS ON ENCAPSULATED EPOXY SYSTEMS

(Effect of epoxy capsules aging on bonding strength)

Curing schedule: 4 hours at 100ºC + 8 hours at 140ºC in all tests

Sample Code	Adhesive System (1) (w/w)	Capsules Storage Environment	Capsules Storage Time(days)	Specimens Number	Shear Strength Mean Values($\bar{x}$) (MPa)	Standard Deviation (σ)	$\sigma/\bar{x}$
BHN-23	A/B(100/22.5)	23ºC/50% RH	3	10	13.1	1.22	0.09
EB 2-4	"	"	150	6	12.1	3.71	0.30
"	"	"	180	6	11.6	1.72	0.15
"	"	"	210	6	11.2	1.16	0.10
"	"	23ºC/85% RH	120	6	13.9	0.72	0.05
"	"	23ºC/70% RH	120	6	13.3	1.06	0.08
"	"	40ºC/85% RH	7	6	15.9	1.08	0.07
"	"	"	30	6	3.2	1.76	0.55
EB 8-1	A/B/C(100/22.5/0.1)	23ºC50%RH	450	10	13.9	1.95	0.14
EB 2-4	A/B(100/22.5)	40ºC/Ultraviolet light	10	6	13.1	1.18	0.09
"	"	"	20	6	13.0	1.45	0.11

(1) Constituent A = Bepox LX/21
Constituent B = Hardener HT 972
Constituent C = Triethanolamine

in which lap shear strengths fairly steady were measured.

Some improvement are observed in shear strengths of samples stored in humid environments. A possible explanation for this fact could be a better anchorage of moist hardener to the capsules surfaces whilst dry hardener's particles have a tendency to settling, difficulting the homogeneity and stability of dry formulations.

With regard to storage at temperature above the ambient, in viewing the Table for samples stored at 40ºC/85% RH, it appears after a short term exposure of 7 days a noticeable improvement in shear strength, giving an average value of 15.9 MPa, that is practically identical as for original unencapsulated samples. This benefitial effect is transient, because after a short time the shear strength is falling down sharply and after one month of exposure the remaining shear strength is only 3.2 MPa.

An excellent long term behaviour was found with a capsular formulation containing minor amounts of triethanolamine as additive. (Sample code EB 8-1). This sample retained unchanged its shear strength after 18 months of storage at standard ambient conditions.

When dealing with Bepox capsules exposed to ultraviolet radiations, some tests were conducted by using the same apparatus as for anaerobic systems. Exposure timings of 250hr and 500hr were scheduled. The samples exposed darkened considerably and capsule's surface became more hard and brittle, although this process did not affect the inside of capsules, because formulations based on these systems show quite good shear strengths, as can be seen in the corresponding figures of Table VI.

It must be noticed that all test results presented in Table VI concern to capsular adhesive systems in which only one constituent, the encapsulated epoxy resin, has been subjected to the environmental aging indicated in that Table. The adhesive systems were prepared in every run by mixing the hardener with the corresponding aged epoxy capsules not more than 24 hours in advance to the bonding process.

Another set of lap shear tests was conducted on fully formulated capsular adhesives subjected as a whole to environmental aging conditions following similar schedules as for the above mentioned tests. The aim of doing these new tests was directed to determine the environmental effect on storage stability of capsular adhesives totally formulated.

The exposure conditions and test results are presented in Table VII. By comparing these results with those of Table VI no significative differences are found. Therefore it can be assumed that when dealing with the epoxy systems used in this Project, similar storage stability is achieved for capsular adhesives when each constituent (hardener and encapsulated resin) are stored separately than if both constituents are previously mixed and the resulting formulation is stored in one can.

This is not applicable to capsular adhesive systems in which HT 972 hardener is anchored on Bepox capsules by using n-butanol as carrier. In this case, diffusion of dissolved hardener through the capsule shell cause its progressive hardening, reducing significatively the storage life of this type of capsular formulation.

TABLE VII-ADHESION TESTS ON AGED CAPSULAR EPOXY SYSTEMS

Curing schedule: 4 hours at 100ºC + 8 hours at 140ºC

Sample Code	Adhesive System(1) (w/w)	Aging Environment	Aging Time(days)	Specimens Number	Shear Strength Mean Values($\overline{x}$) (MPa)	Standard Deviation (σ)	$\sigma/\overline{x}$
F 21	A/B(100/22'5)	23ºC/50% RH	42	5	10.6	0.99	0.09
F 21	"	"	120	8	10.7	0.60	0.06
F 22	"	23ºC/70% RH	35	5	14.2	0.82	0.06
F 22	"	"	115	5	15.3	1.08	0.07
F 23	"	23ºC/85% RH	35	5	14.0	0.79	0.06
F 23	"	"	50	6	13.0	1.17	0.09
F 23	"	"	120	6	12.8	1.28	0.10

(1) Constituent A = Bepox LX/21
Constituent B = Hardener HT 972

E - Characterization of raw materials and capsular adhesives by Liquid Chromatography and Infrared Spectroscopy. Ageing studies.

As outlined in previous Sections, a major objective of this Project was to asses the stability of the resulting microencapsulated adhesives because in many cases this could be the limiting factor for developing capsular adhesive systems.

In precedent chapters have been discussed the stability studies conducted on both anaerobic and epoxy encapsulated adhesives. Those studies were based on periodical evaluations of capsules core contents and bonding strength of samples that have been submitted to ambient ageing in different environmental conditions.

The mentioned stability studies have been completed with an extensive chemical characterization of raw materials and capsular adhesives by using liquid chromatography and infrared techniques, in order to correlate physical and bonding variations caused by ageing processes with chemical changes in those compositions.

In order to get a comparison basis for stability studies and also for evaluation purposes, the characterization of raw materials and adhesive systems in their original conventional form was also fulfilled. The work conducted to achieve the objectives outlined above is presented in the following paragraphs.

The high resolution chromatographic separations (HPLC and GPC) have been performed in a Waters Associated modular system equipped with two pumps (M-45 and M-6000 A), a solvent programmer mod. 660, UV detector M 441 provided with a mercury lamp at 254 nm and a zinc lamp at 214 nm, refractive index detector R 401, injector U6K, integra-

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ting recorder Data Module.

Columns, solvents and flow rates used are indicated in each application. All solvents are HPLC grade and are filtered through PTFE before using.

Low pressure liquid chromatography tests were carried out in glass columns 150 mm x 6 mm i.d. filled with silica gel 70 - 230 mesh. Silica gel is activated in oven at 350ºC during 3 hours. The eluotropic solvents are p.a. grade. The collected fractions were dried at 60ºC during 24 hours in oven for solvent removal, and then were weighted the extracts and its IR spectra recorded on a Perkin Elmer 1420 or 683 apparatus.

1. Study of Loctite 270 and Loctite 290 by HPLC in reverse phase.

A Radial-pack C 18 column was used, with acetcnitrile as mobil phase. The experimental conditions were: acetonitrile gradient profile, from 0.5 ml/min. to 2 ml/min. in 15 minutes, and then maintenance of steady flow until chromatogram completion. UV detection at 214 nm as well as 254 nm was used.

Solutions were prepared with 60 - 80 mg of sample in 25 ml acetonitrile. It was observed that Loctite 290 was totally dissolved whilst Loctite 270 did not. Solutions were all filtered before injecting. The injection volume was in the range of 5 ÷ 25 μl.

In regard to the incomplete solubility of Loctite 270, it is assumed that the insoluble portion of this adhesive concerns the high molecular polymeric constituent, included in the composition as thickening agent, because the presence of such a thickener is the major difference found in comparing Loctite 270 with Loctite 290. It is also assumed that the rest of constituents are all soluble in acetonitrile, as for Loctite 290.

In figures 12 to 15 are presented the chromatograms of both adhesive systems obtained in the above mentioned conditions. Figures 12 and 13 show the chromatograms of Loctite 290 and Loctite 270 respectively at a wavelength of 214 nm. Figures 14 and 15 show the corresponding chromatograms at 254 nm. All peaks have been numbered with the same code, and this numeration code will be used as reference in this chapter.

When comparing the chromatograms it can be seen that some peaks are more apparent at 214 nm (e.g. peaks n 3,4,5,11,14 and 16), while others, like peaks 7,8,9, 9' and 15 have better response at 254 nm.

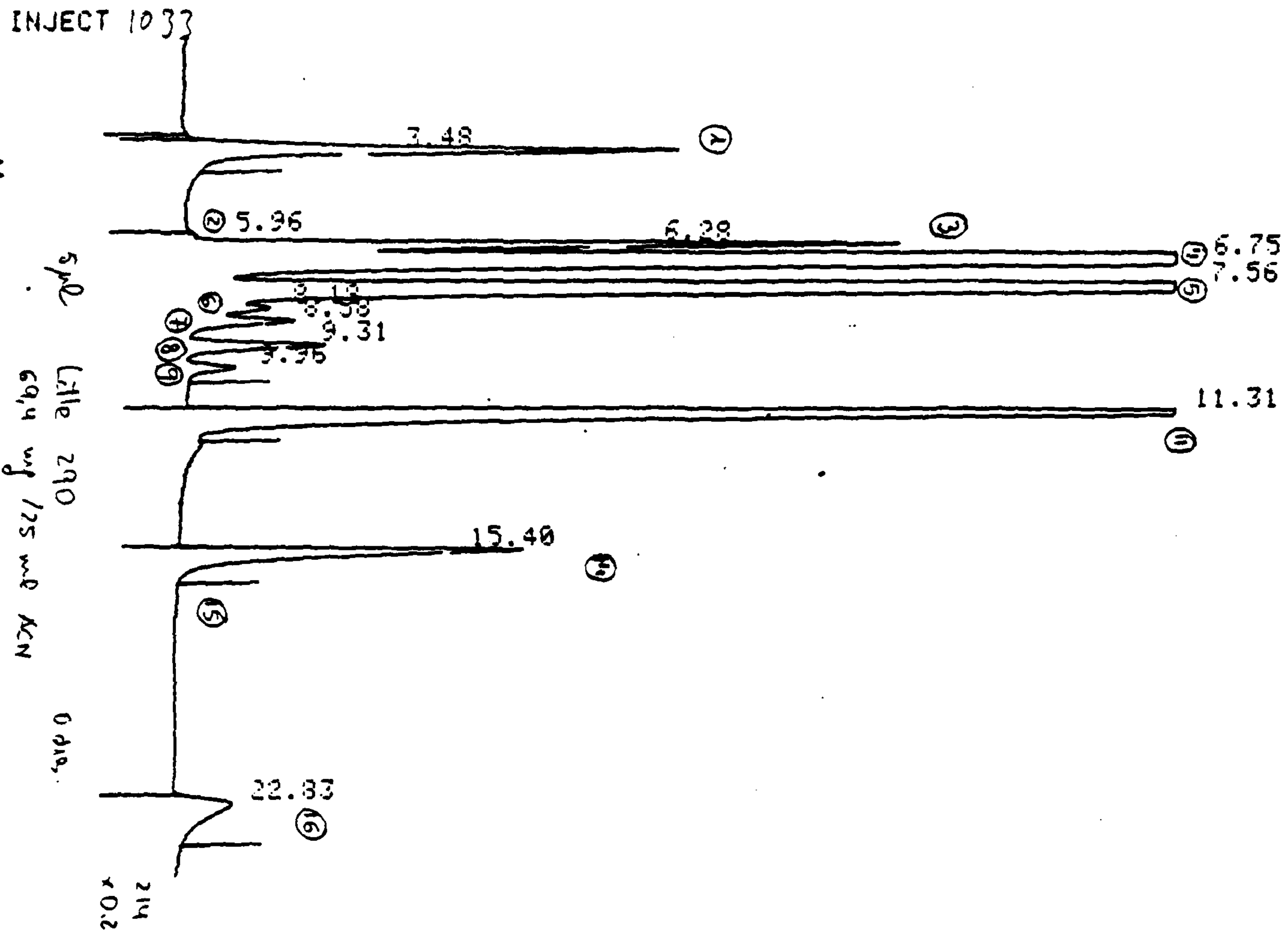
The major difference between HPLC chromatograms for Loctite 270 and Loctite 290 concerns the relative intensity of peak 1. This peak is more intense for Loctite 270 than for Loctite 290. There are also other minor differences in peaks 7 and 8. Both of them are slightly higher for Loctite 270.

In order to investigate on peaks assignations for the above mentioned chromatograms, low pressure chromatographic separations were carried out, as described below.

2. Low pressure column chromatographic studies on Loctite 270 and Loctite 290.

Low pressure chromatographic fractionations were conducted by using a glass column filled with activated silica gel as described in page 50. For each adhesive system

WATERS DATA MODULE

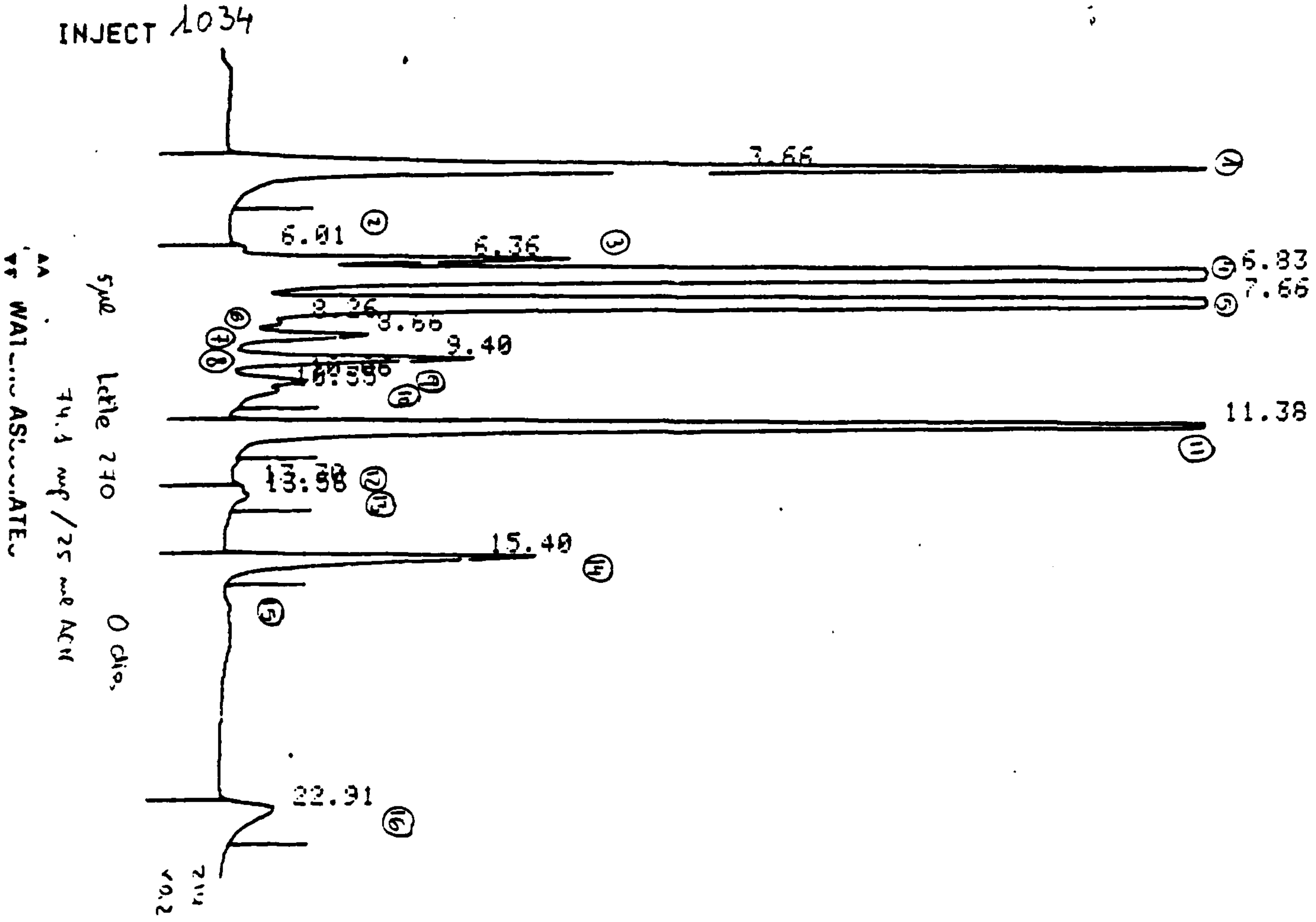


```
                                     CHART  0.50 CM/MIN
                                     RUN #1                        CALC #0
COLUMN                               SOLVENT                     OPR ID:       5

EXTERNAL STANDARD QUANTITATION

 PEAK#           AMOUNT        RT      EXP RT       AREA              RF
            6429.97000       3.48                6430004 L    0.000000E0
             119.30400       5.96                 119304 F    0.000000E0
            7919.82000       6.28                7919857 F    0.000000E0
           96716.10000       6.75               96716839 F    0.000000E0
           62158.50000       7.56               62158966 F    0.000000E0
            1230.74000       8.18                1230746 F    0.000000E0
            1507.95000       8.58                1507960 F    0.000000E0
            1779.89000       9.31                1779898 F    0.000000E0
             581.60000       9.96                 581600 L    0.000000E0
           23738.60000      11.31               23738794 L    0.000000E0
            5640.58000      15.40                5640609 L    0.000000E0
            2164.21000      22.83                2164219 L    0.000000E0
TOTAL     209989.00000
```

Figure 12 - Chromatogram for Loctite 290 at 214 nm wavelength.

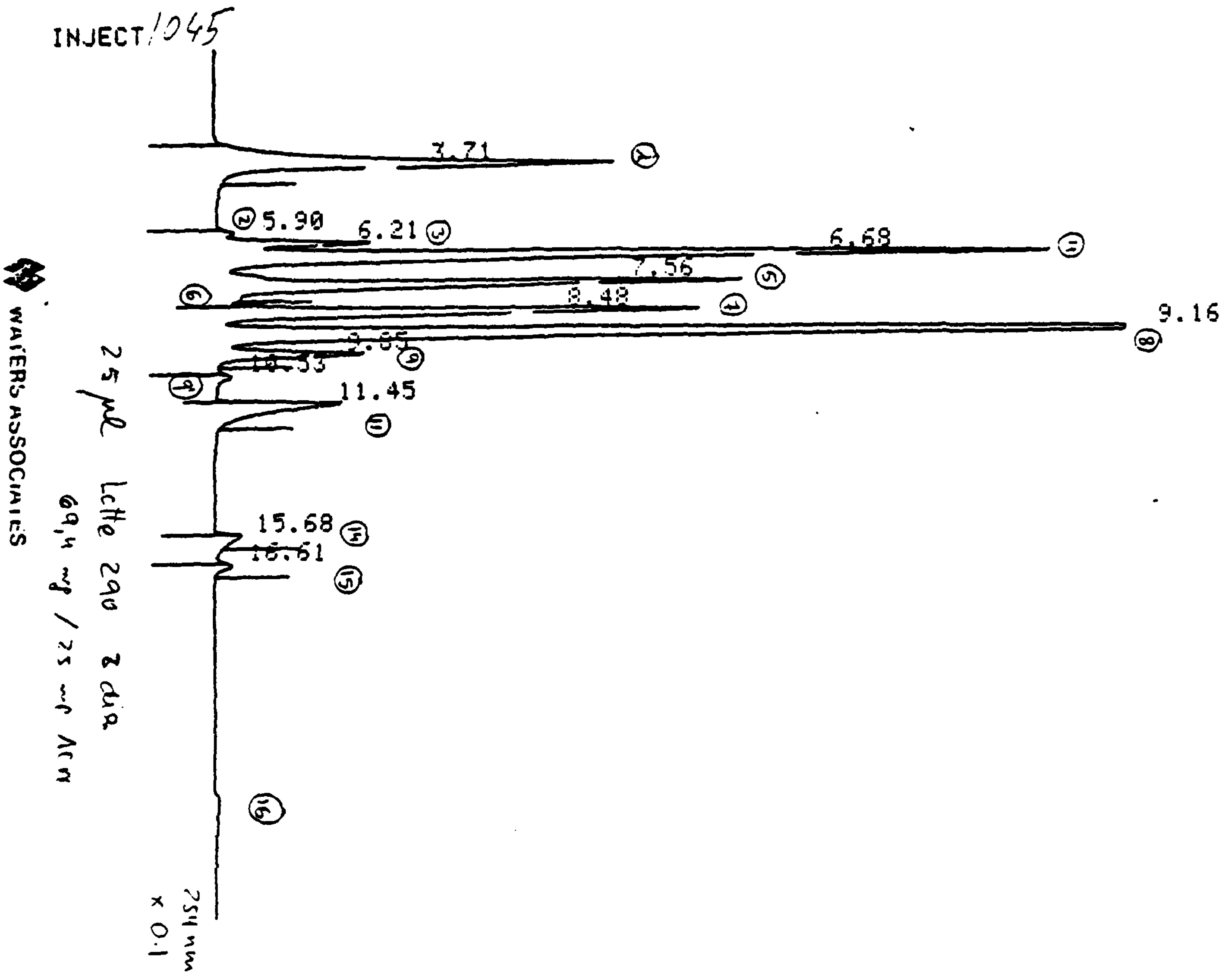


```
                                   CHART  0.50 CM/MIN
                                   RUN #2                        CALC #0
COLUMN                             SOLVENT                    OPR ID:      5

EXTERNAL STANDARD QUANTITATION

 PEAK#           AMOUNT       RT     EXP RT      AREA             RF
             16704.20000     3.66     21.4    16704313 L    0.000000E0
               174.53600     6.01               174536 F    0.000000E0
              3368.22000     6.36      5.0     3368241 F    0.000000E0
             78124.10000     6.83     100     78124674 F    0.000000E0
             53025.30000     7.66      63     53025624 F    0.000000E0
               623.45200     8.26               623452 F    0.000000E0
              1947.97000     8.66              1947976 F    0.000000E0
              3192.18000     9.40              3192201 F    0.000000E0
              1010.16000    10.06              1010160 F    0.000000E0
               673.54200    10.35               673542 L    0.000000E0
             20676.80000    11.38     26.5    20676971 L    0.000000E0
               108.22000    13.30               108220 F    0.000000E0
               271.48600    13.56               271486 L    0.000000E0
              5161.77000    15.40      6.6     5161789 L    0.000000E0
              1843.47000    22.91      2.4     1843478 L    0.000000E0
TOTAL       137404.00000
```

Figure 13 - Chromatogram for Loctite 270 at 214 nm wavelength.

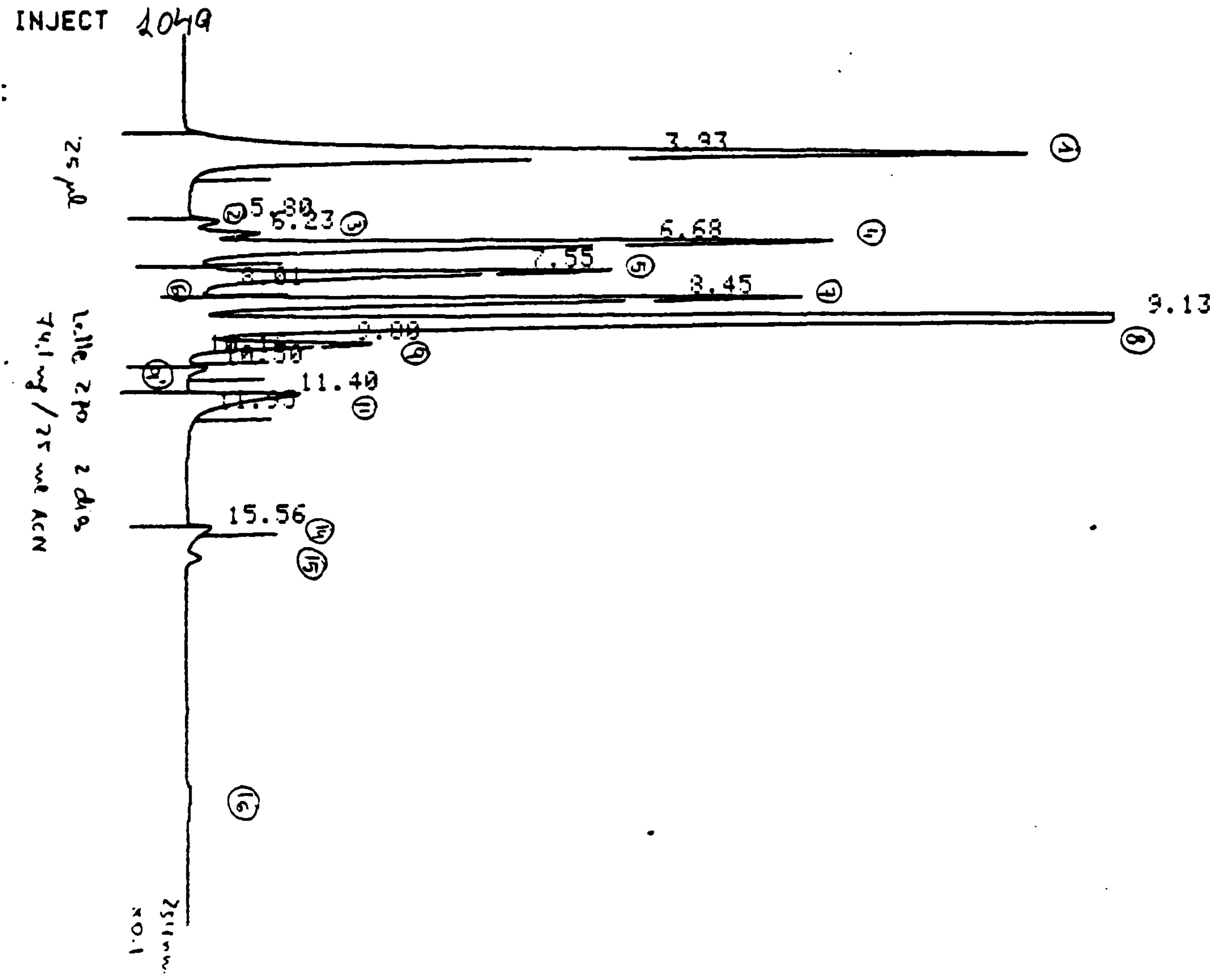


```
                                        CHART  0.50 CM/MIN
                                        RUN #3                        CALC #0
COLUMN                                  SOLVENT                     OPR ID:       5

EXTERNAL STANDARD QUANTITATION

 PEAK#            AMOUNT        RT       EXP RT        AREA                RF
               3717.09000     3.71                   3717106 L     0.000000E0
                 97.37100     5.90                     97371 F     0.000000E0
                901.72500     6.21                    901725 F     0.000000E0
              [6333.62000]   [6.68                   6333654 F     0.000000E0
              [3597.80000]   [7.56                   3597820 L     0.000000E0
               3143.10000     8.48                   3143119 F     0.000000E0
              10293.10000     9.16                  10293176 F     0.000000E0
                954.53900     9.85                    954539 L     0.000000E0
               1176.63000    11.45                   1176640 L     0.000000E0
                139.99600    15.68                    139996 L     0.000000E0
                114.70300    16.61                    114703 L     0.000000E0
TOTAL         30469.60000
```

Figure 14 - Chromatogram for Loctite 290 at 254 nm wavelength.



```
                                   CHART  0.50 CM/MIN
                                   RUN #8                         CALC #0
COLUMN                             SOLVENT                      OPR ID:      5

EXTERNAL STANDARD QUANTITATION

 PEAK#             AMOUNT       RT       EXP RT        AREA            RF
               8747.96000      3.93                 8748010 L    0.000000E0
                144.91900      5.30                  144919 F    0.000000E0
                373.89500      6.23                  373895 F    0.000000E0
               4790.77000      6.68                 4790796 L    0.000000E0
               2728.83000      7.55                 2728841 F    0.000000E0
               4149.03000      8.45                 4149053 F    0.000000E0
              17558.40000      9.13                17558559 F    0.000000E0
               1211.31000      9.80                 1211319 F    0.000000E0
                ~~76.~~31200     10.50                   76812 L    0.000000E0
               1080.60000     11.40                 1080602 F    0.000000E0
                  9.32400     11.95                    9324 L    0.000000E0
                 85.24900     15.56                   85249 L    0.000000E0
TOTAL         40956.90000
```

Figure 15 - Chromatogram for Loctite 270 at 254 nm wavelength.

a solution in carbon tetrachloride was prepared and a portion of 300 to 500 mg was introduced into the columns in which a number of fractions were eluted by means of the following eluotropic solvents serie:

1) Carbon tetrachloride ($C Cl_4$)
2) Benzene
3) Methylene chloride ($CH_2 Cl_2$)
4) $C Cl_4/CH_2 Cl_2$ (1:1 v/v)
5) Ethyl ether/$CH_2 Cl_2$ (1:1 v/v)
6) Acetone/ethyl ether (1:1 v/v)
7) Methanol

Individual fractions were collected and, after solvent removal at 60ºC, each residue was weighted and its IR spectrum registered, when feasible, by deposition on Na Cl disks.

The summation of individual residues totalized roughly 95% of original samples in most cases, giving an indication of satisfactory fractions recovery.

HPLC chromatograms were carried out on each significative fraction and these chromatograms were checked against the chromatogram of the whole adhesive.

In Figures 16 to 20 are shown the more representative IR spectra of the fractions obtained as indicated.

The spectrum of Figure 16 shows the product collected in the initial fractions of Loctite 270 and it looks like an epoxy/polyester mixture. The total amount for these fractions represents 8% approx., for Loctite 270, whereas for Loctite 290, do not surpass 0'5%. It is assumed that these fractions in which are found the major differences between Loctite 270 and Loctite 290,

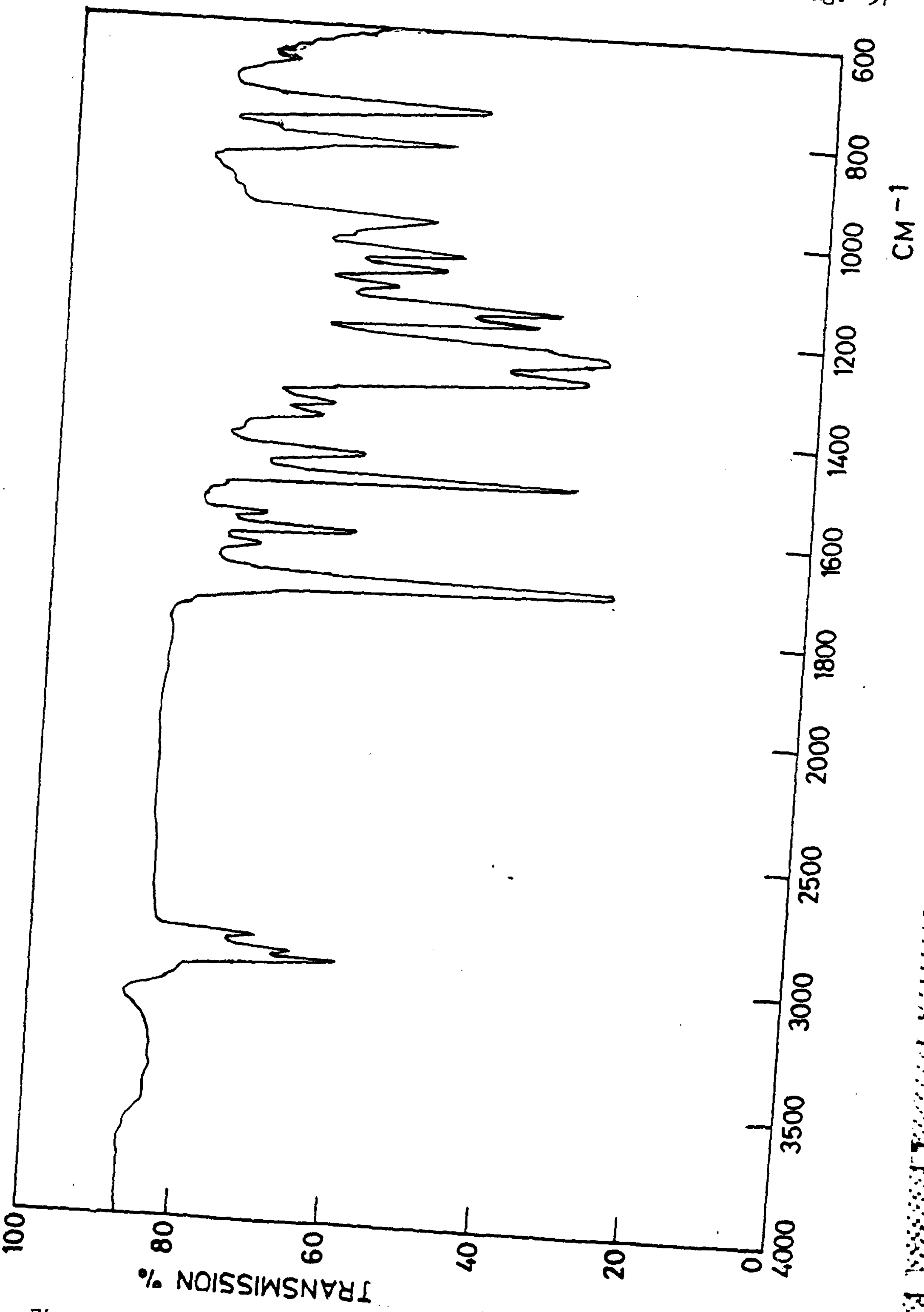


Figure 16 - IR spectrum for fraction eluted with carbon

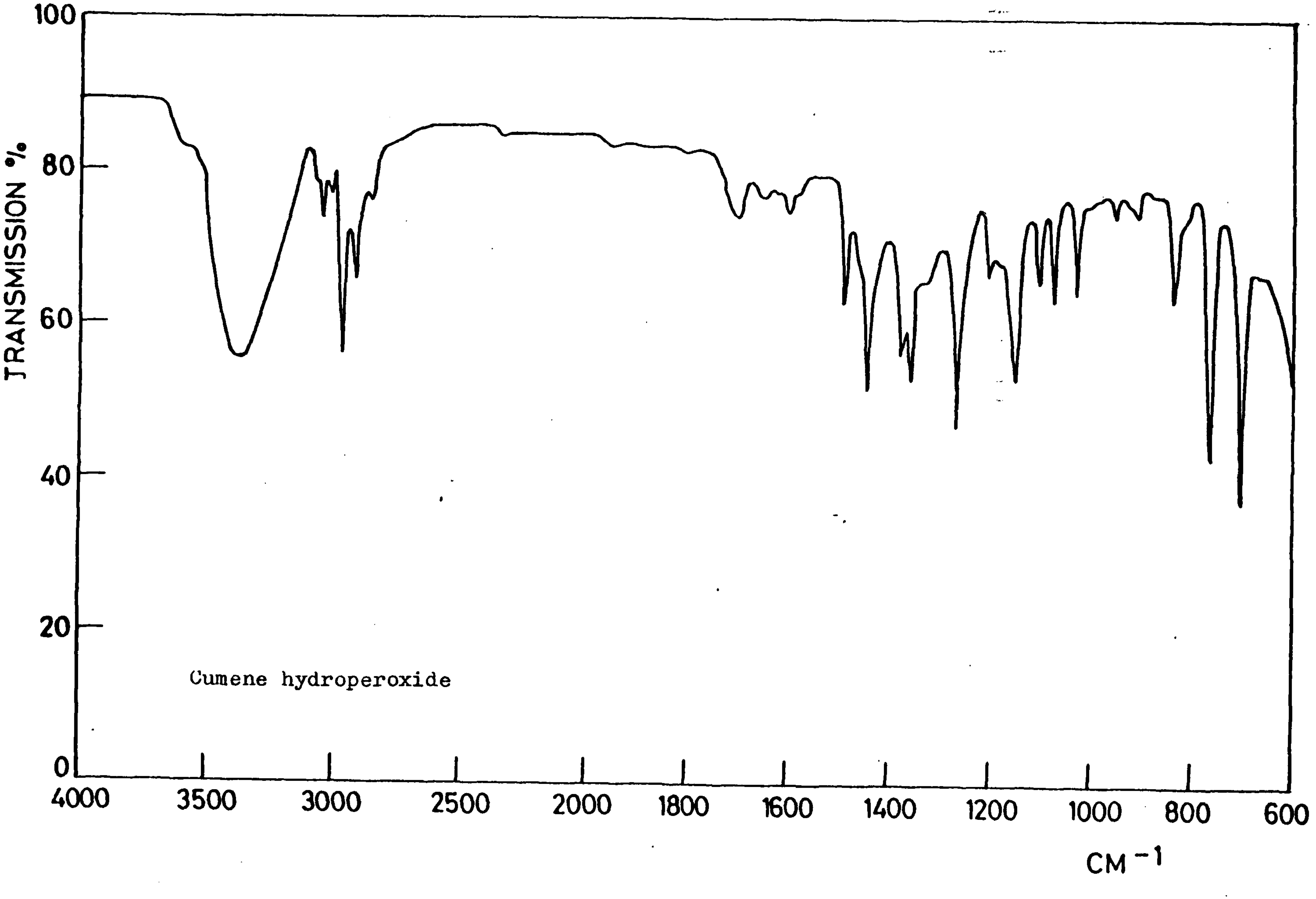


Figure 17 - IR spectrum for fraction eluted with benzene.

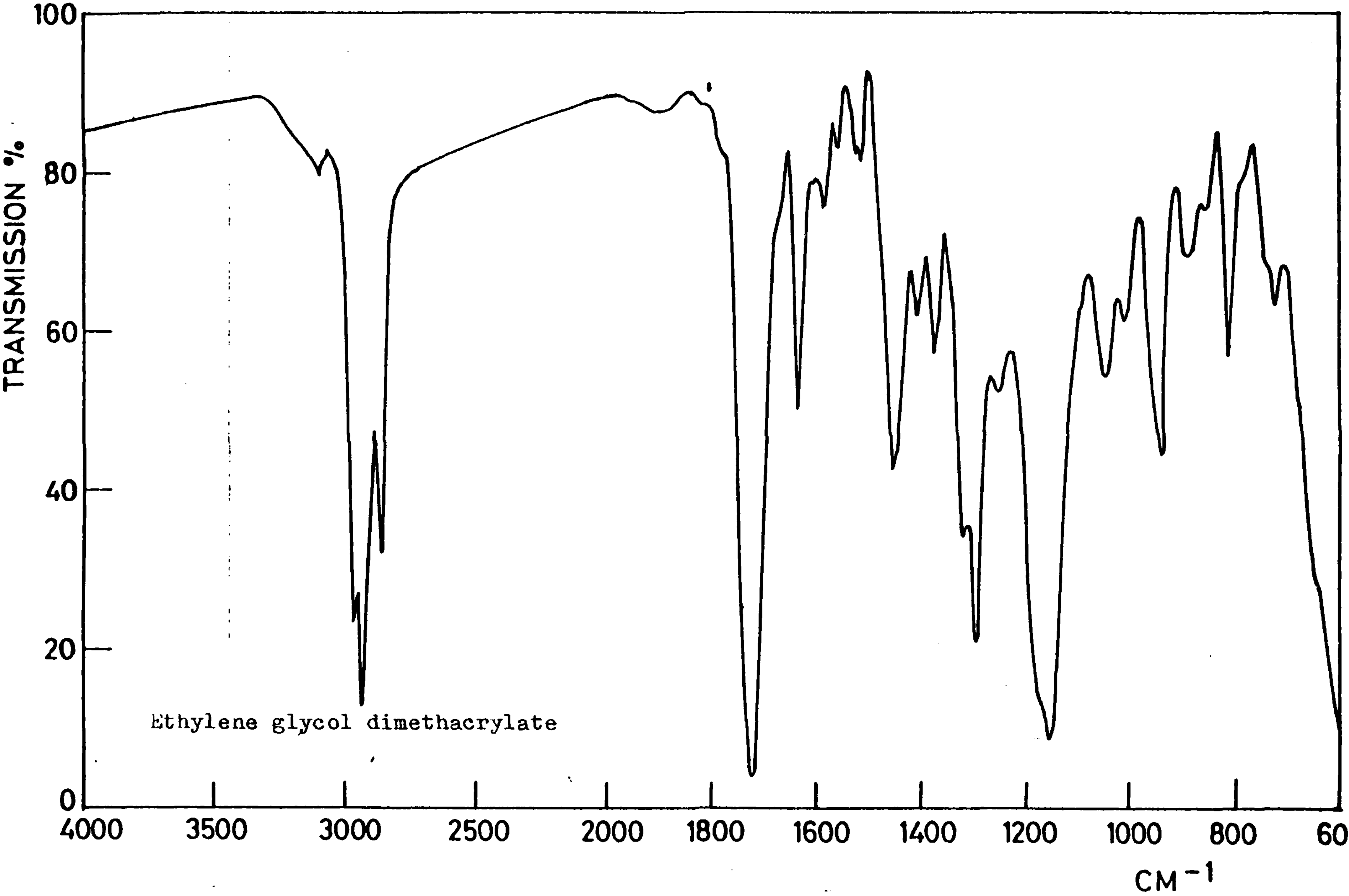


Figure 18 - IR spectrum of fraction eluted with methylene chloride.

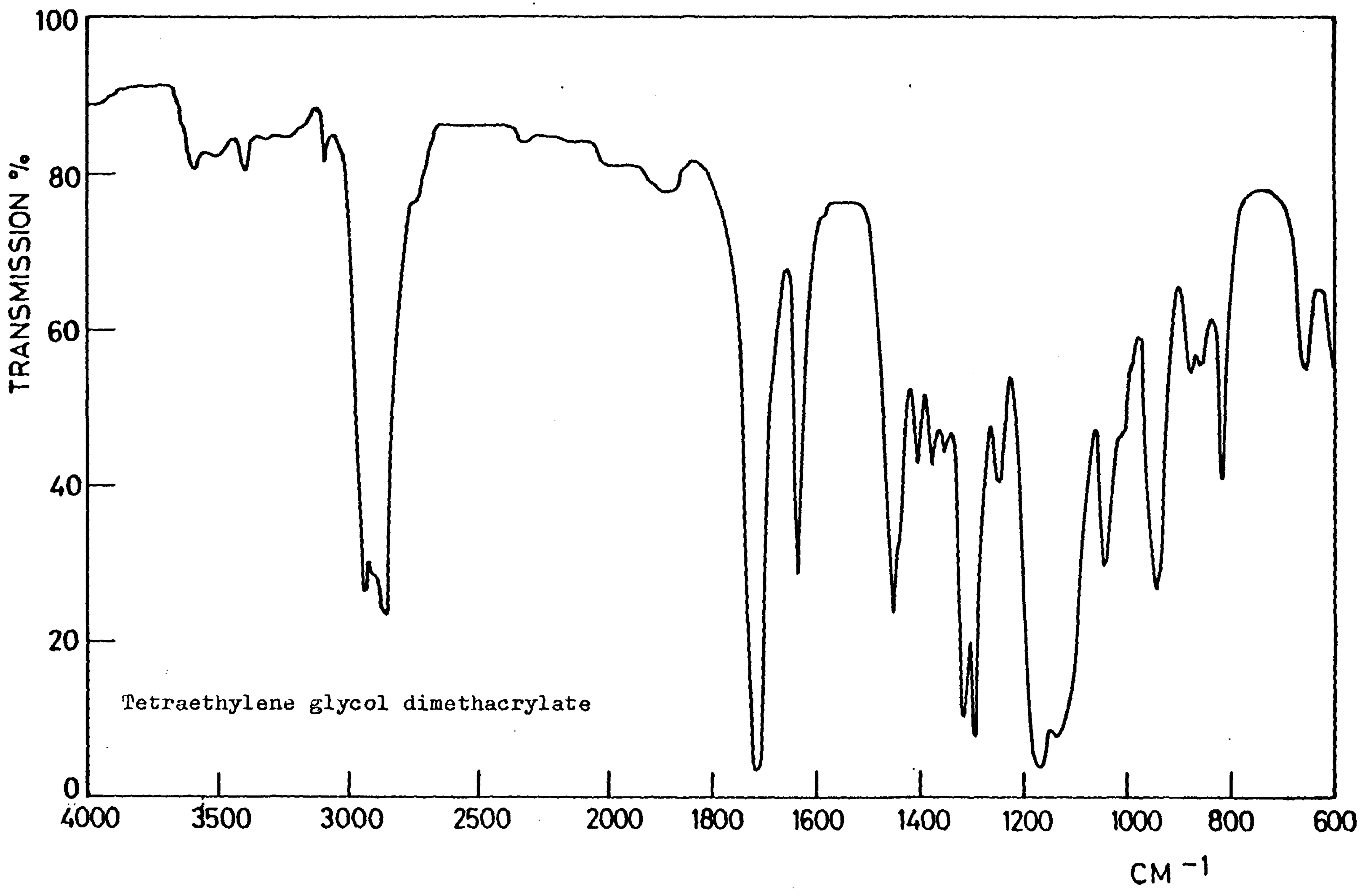


Figure 19 - IR spectrum of fraction eluted with ethyl ether/methylene chloride.

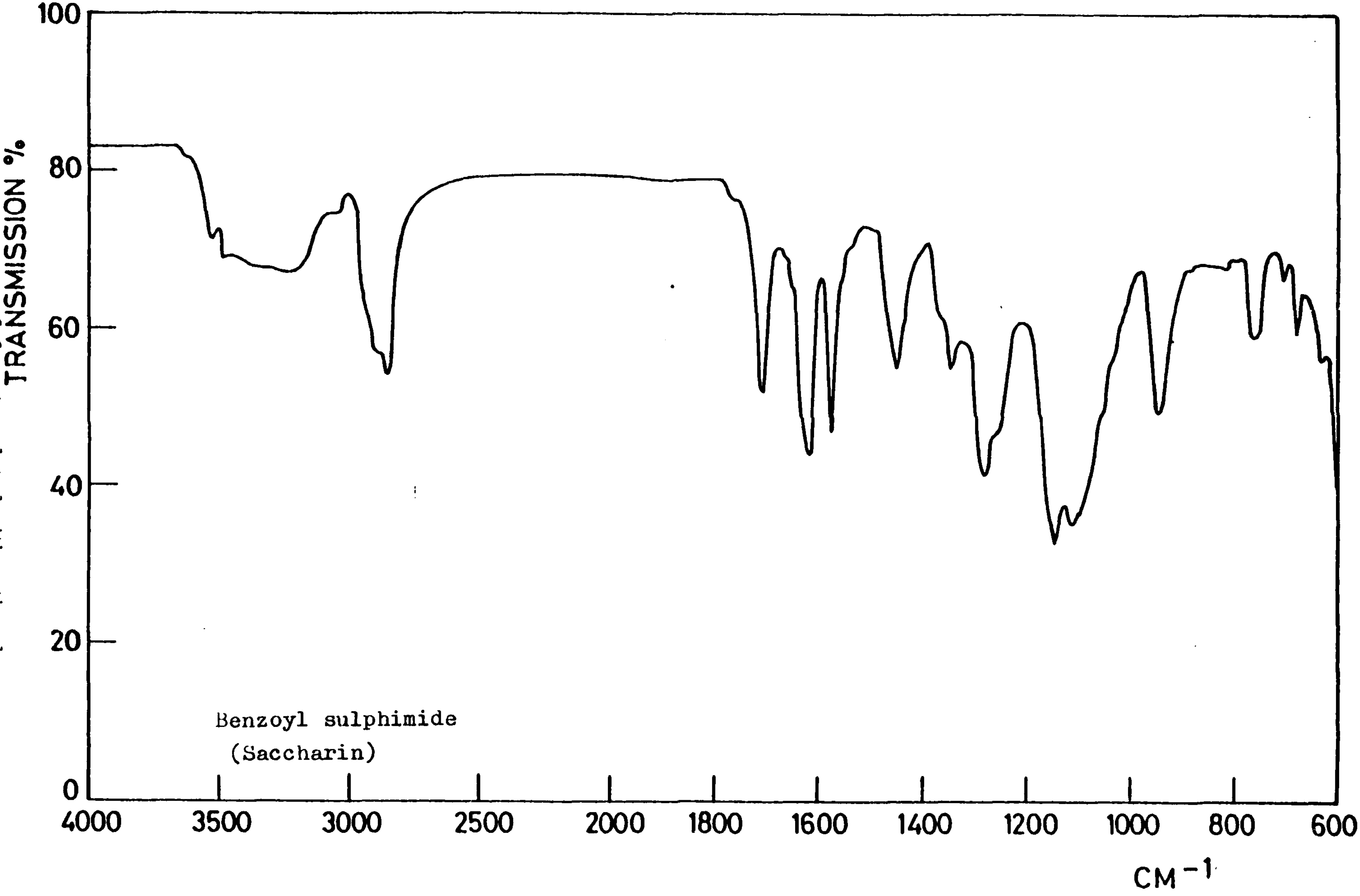


Figure 20- IR spectrum of fraction eluted with methanol.

are constitued mainly by polymeric thickener. The chromatograms for these initial fractions show the presence of peaks 1, 9 and 9', the first one being in very high ratio with regard to the others.

In Figure 17 can be seen the IR spectrum of a substance collected in some fractions when benzene is used as eluent. The feature of this spectrum indicates that the major constituent of this fraction is cumene hydroperoxide, that is commonly used as polymerization initiator. The chromatograms for these fractions are formed basically with two peaks, the coded with number 9 as more relevant and the less apparent peak 9'. Therefore these peaks are assigned to cumene hydroperoxide.

Figure 18 shows the IR spectrum of a fraction eluted with methylene chloride. This spectrum shows the feature of a low molecular ethylene glycol dimethacrylate. It is assumed, consequently that this monomer is a constituent in the polymerizable composition of the studied anaerobic systems. The chromatogram for this fraction is formed almost exclusively with peak 3.

Figure 19 shows a typical spectrum for the product collected in fractions eluted with the mixture ethyl ether/methylene chloride. In these fractions are collected the major constituents of the polymerizable compositions. The IR spectrum showed in Figure 19 presents a very close coincidence with tetraethylene glycol dimethacrylate (Sadtler Collection IR spectrogram D 4058). Therefore it is assumed that both systems, Loctite 270 and Loctite 290 are based on this monomer as main constituent for the polymerizable composition. The chromatogram for this fraction is more complex than the former ones. Peaks 4,5,11,14 and 16 are present for Loctite 290 and the same peaks with the addition of peaks 1 and

8 are observed for Loctite 270.

Finally in Figure 20 can be seen the IR spectrum for the fraction collected with the more polar eluent: methanol. This spectrum is in good agreement with the one corresponding to saccharin (benzoyl sulphimide). Since this substance can be used as latent accelerator for anaerobic adhesives, it is assumed that this chemical has been efectively used in Loctite 270 and Loctite 290 compositions. HPLC chromatogram for this fraction did show almost exclusively peak 1, with other weak peaks from monomers being present.

In order to complete the chromatographic peaks assignation, samples of NN dimethyl-o-toluidine and NN diethyl-p-toluidine, (commonly used as latent accelerator for anaerobic systems) were injected as external standards and thus peaks 7 and 8 were identified as belonging to these additives.

According with the results achieved in this study, the following chromatographic assignations are proposed for Loctite's adhesives:

Chromatographic data

Peak	Retention time (min)	Assignation
1	3.5	a) Polymeric thickener (epoxy/polyeter) (For Loctite 270) b) Benzoyl sulphimide
2	6.0	Unidentified (very weak peak)
3	6.3	Ethyleneglycol dimethacrylate
4	6.8	Polyethylene-glycol dimethacrylate
5	7.7	" " "
6	8.3	Unidentified (weak peak)

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Chromatographic data

Peak	Retention time (min)	Assignation
7	8.6	NN' dimethyl-o-toluidine
8	9.2	NN' diethyl-p-toluidine
9 9'	9.8 10.5	Cumene hydroperoxide
10	10.3	For Loctite 270. Unidentified
11	11.5	Polyethylene glycol dimethacrylate
12		
13	13.5	Unidentified (traces only in Loctite 270).
14	15.4	Polyethylene glycol dimethacrylate
15	16.6	Coloring agent
16	22-25	Polyethylene glycol dimethacrylate

The above listed peaks assignation served as reference basis for further characterization and control studies as will be disclosed in the following paragraphs.

3 - Chromatographic profiles and composition evaluations for unencapsulated Loctite adhesives.

On the basis of the peaks assignation previously described, chromatographic "profiles" can be defined for both Loctite systems by making two peaks groups, the first one with those assigned to major constituents (polymerizable basis), and the second one with minor constituents (additives) peaks.

The "basic" profile is formed with peaks 1,3,4,5,11,14 and 16 from chromatograms at 214 nm. The area ratios for these peaks are calculated taking the most intense (4) as reference. For comparative evaluations a titration of peak 4 is performed by using the chromatographic

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fraction collected with ethylether/methylene chloride in which peak 4 appears as major constituent and additive's peaks are not present. For this comparative evaluation it is assumed the same detector response for all peaks in this group.

The "additives" profile is formed with peaks 7, 8, 9, 9' and 15 from chromatograms at 254 nm. Peak 1 is also included although there is a contribution of polymeric thickener in it, because is partially assigned to benzoyl sulphimide (latent accelerator).

The area ratios for these peaks are calculated with the same reference as before (peak 4). Looking at the diverse chemicals present in this composition, different detector response is expected for each additive and therefore no real values can be obtained unless suitable external or internal standards are available. In this study, N-N dimethyl-o-toluidine and N-N diethyl-p-toluidine were used as external standards for evaluation of peaks 7 and 8 respectively.

By using this approach to following profiles were obtained for the original adhesives.

a) Major constituents (polimerizable basis).

(Peak)	(1)	(3)	(4)	(5)	(11)	(14)	(16)
Loctite 270	21	5	100	67	26	6	2
Loctite 290	7	8	100	64	24	6	2

b) Minor constituents (additives).

(Peak)	(1)	(4)	(7)	(8)	(9)	(9')	(15)
Loctite 270	180	100	86	360	25	2	2
Loctite 290	58	100	50	163	15	1.5	2

On the basis of these profiles and using the above mentioned internal and external standards for quantitative evaluations, the following theoretical compositions have been estimated:

	Loctite 270	Loctite 290
Polymerizable dimethacrylate ether	67% W	92% W
Polymer thickeners and plasticizers	25% W	0% W
Cumene hydroperoxide	3.6% W	3.0% W
Diethyl-p-toluidine	0.9% W	0.6% W
Dimethyl-[illegible]-toluidine	0.3% W	0.2% W
Benzoyl sulphimide	3.0% W	3.0% W
Dye,stabilizers	0.5% W	0.5% W

4 - Control of encapsulated Loctite adhesives by liquid chromatography. Stability studies.

The chromatographic procedures developed to evaluate unencapsulated Loctite systems were used as analytical tool for control of encapsulated adhesives and for stability studies on these capsular systems.

With regard to adhesives control, this involves both, qualitative and quantitative aspects. Quality controls are conducted by comparing the profiles of capsules core contents with the same system in its original form. Quantitative control implicates also the capsules active contents titration by using as standards the correlated original adhesives.

In order to get consistent results, complete extractions of capsules contents are required. A satisfactory procedure to do that, was by rupturing the capsules immersed in acetonitrile (chromatographic solvent) with the

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aid of an ultrasonic bath.

This study was conducted on four sets of encapsulated adhesives belonging to the different types of capsular systems obtained, that's to say, Loctite 270 encapsulated by using sodium bisulphite as catalyst (Code: Mc 270 B); Loctite 270 encapsulated with Redox catalyst (Code: Mc 270 R); Loctite 290 encapsulated with sodium bisulphite (Code: Mc 290 B) and Loctite 290 encapsulated with Redox system (Code: Mc 290 R). Aliquots of the above mentioned capsules runs were subjected to ambient ageing in the following environmental conditions:

a) Under ultraviolet light at 40ºC ± 2ºC for 72 hours (UV energy level 1.6 W in the range of 280 - 350 nm).

b) at 40ºC ± 2ºC and 85% ± 5% RH during a period of 6 weeks.

These aged samples were also subjected to chromatographic analysis in order to follow the composition changes induced by the ageing processes. For identification purposes the samples axposed to ultraviolet radiations will be designated with the letters UV after its original code and, similarly, the samples exposed in hot-wet ambient conditions will be identified by the letters HW after its code.

By using the same experimental procedures as for the unencapsulated systems, the chromatographic profiles for major constituents and for additives were obtained on each encapsulated sample. In Tables VIII to XI are schematically presented the profiles of the different samples studied. For facilitating comparative evaluations in each Table is also included the profil of the original unencapsulated adhesive system.

For an easier survey of these Tables, in Figures 21 to 24 are graphically presented the profiles for the samples studied.

In viewing these Tables and Figures the following conclusions are apparent:

a) When encapsulated, Loctite 270 maintains better its original basic composition that Loctite 290 does (see profiles in Tables VIII and IX).

b) Microencapsulation has a marked effect on reducing the level of toluidines in the composition. This effect can be observed for both Loctite systems although is more noticeable for Loctite 290. Finally this effect is more pronounced when dealing with microcapsules obtained by using Redox systems (see ratios of peaks 7 and 8 in Table X and XI).

c) UV light hardens the capsules, diminishing its active contents substantially and converting then useless in short time. This phenomenon is more pronounced for Loctite 290 than for Loctite 270. These results are in good agreement with those disclosed in Section C.1 of this Report. (see pages 29-31).

d) The "gain of weight" phenomenon upon high humidity environments exposure, that was observed in previous aging tests (see Section C.1) is confirmed by the results of chromatographic analysis which shows a gain in core contents, at least for Loctite 290 encapsulated by bisulphite catalyst. This effect must be caused by moisture absortion and diffusion through the capsule's shell, allowing some limited hydrolysis reactions e.g. with toluidines, that are very sensitives to UV or moist ambients.

TABLE VIII - COMPARATIVE LC PROFILES (AT 214 nm) FOR MAJOR CONSTITUENTS OF ENCAPSULATED LOCTITE 270.

Peaks	1	3	4	5	11	14	16	Active Contents
L 270 original	21	5	100	67	26	6	2	100% wt
Mc 270 R	14.2	3.95	79	51.3	19.8	4.74	--	79% wt
Mc 270 R-H	7.4	--	67	42.9	14.7	3.35	0.67	67% wt
Mc 270 R-UV	10.6	1.77	59	40.1	15.3	3.54	--	59% wt
Mc 270 B	16.4	3.64	91	59	21.8	5.5	--	91% wt
Mc 270 B-H	11.8	--	84	55.4	20.2	5.04	--	84% wt
Mc 270 B-UV	14.1	2.22	74	51.1	17.8	4.4	--	74% wt

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TABLE IX - COMPARATIVE LC PROFILES (AT 214 nm) FOR MAJOR CONSTITUENTS OF ENCAPSULATED LOCTITE 290.

Peaks	1	3	4	5	11	14	16	Active Contents
L 290 original	7	8	100	64	24	6	2	100% wt
Mc 290 R	2.85	6.7	95	49.4	15.2	2.85	--	95% wt
Mc 290 R-H	1.88	--	94	55.5	16.0	2.82	--	94% wt
Mc 290 R-UV	0.78	--	3	1.38	0.39	--	--	3% wt
Mc 290 B	2.43	5.67	81	48.6	17.0	4.1	--	81% wt
Mc 290 B-H	1.72	--	86	57.6	19.8	4.3	--	86% wt
Mc 290 B-UV	0.9	0.3	10	5.2	1.6	0.3	--	10% wt

TABLE X - COMPARATIVE LC PROFILES (AT 254 nm) FOR ADDITIVES OF ENCAPSULATED LOCTITE 270.

Peaks	1	4	7	8	9	9'	15	Active Contents
L 270 original	180	100	86	360	25	2	2	100% wt
Mc 270 R	94	79	20.5	194	26.9	1.6	1.6	79% wt
Mc 270 R-H	54	67	0	1.3	21.4	2.0	1.3	67% wt
Mc 270 R-UV	110	59	0	1.8	3.5	0	--	59% wt
Mc 270 B	141	91	49	298	27.3	2.7	--	91% wt
Mc 270 B-H	81	84	0	42	20.2	1.7	1.2	84% wt
Mc 270 B-UV	104	74	5.2	15.5	6.7	0	1.1	74% wt

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TABLE XI - COMPARATIVE LC PROFILES (AT 254 nm) FOR ADDITIVES OF ENCAPSULATED LOCTITE 290.

Peaks	1	4	7	8	9	9'	15	Active Contents
L 290 original	58	100	50	163	15	15	2	100% wt
Mc 290 R	16	95	0	8	19	1.9	2.9	95% wt
Mc 290 R-H	13	94	0	0	23.5	1.9	1.9	94% wt
Mc 290 R-UV	7.1	3	0	0	0	0	0	3% wt
Mc 290 B	18.6	81	12.2	50.2	14.6	1.3	1.6	81% wt
Mc 290 B-H	12.9	86	0	4.3	16	1.7	1.3	86% wt
Mc 290 B-UV	6.4	10	1.2	5.3	0	0.8	0	10% wt

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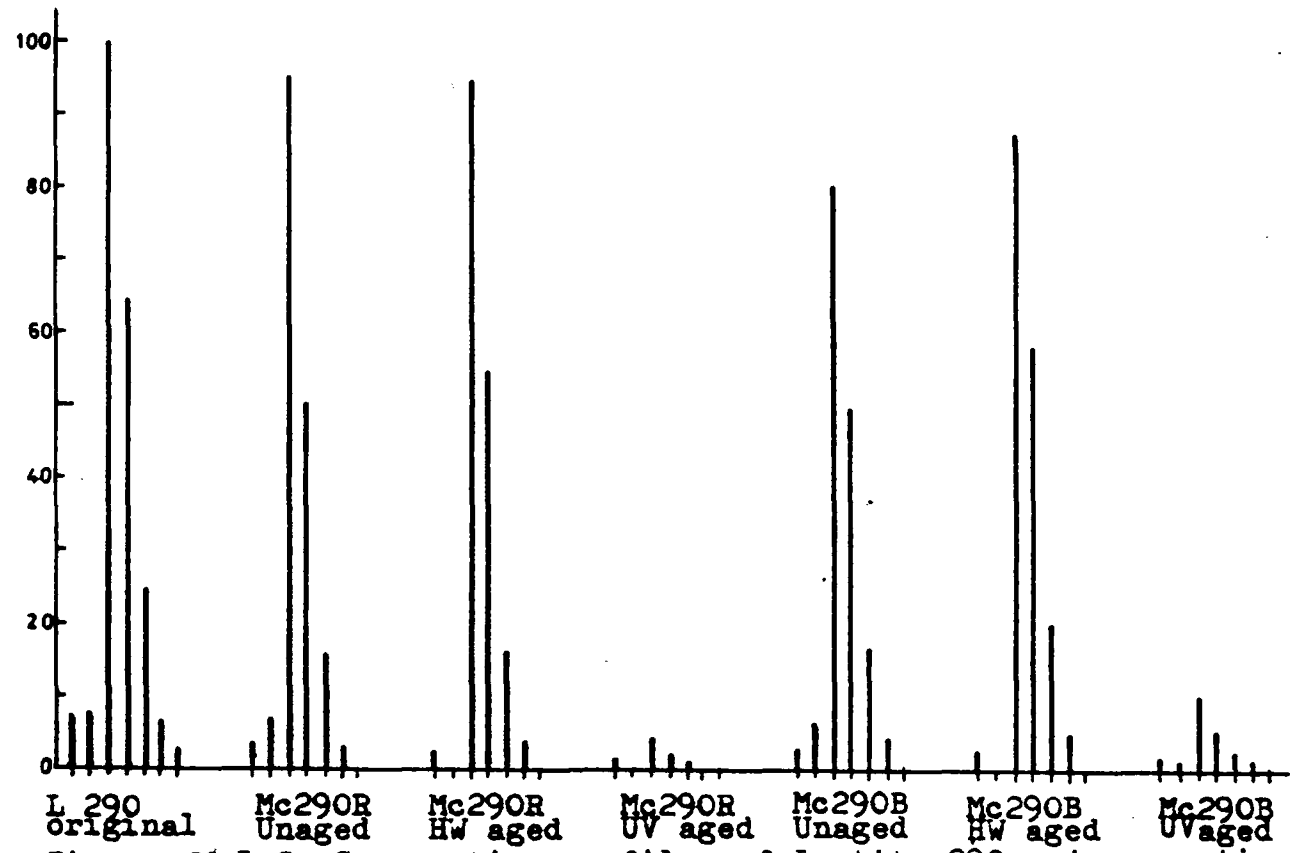

Figure 21 L.C. Comparative profiles of Loctite 290 major constituents.

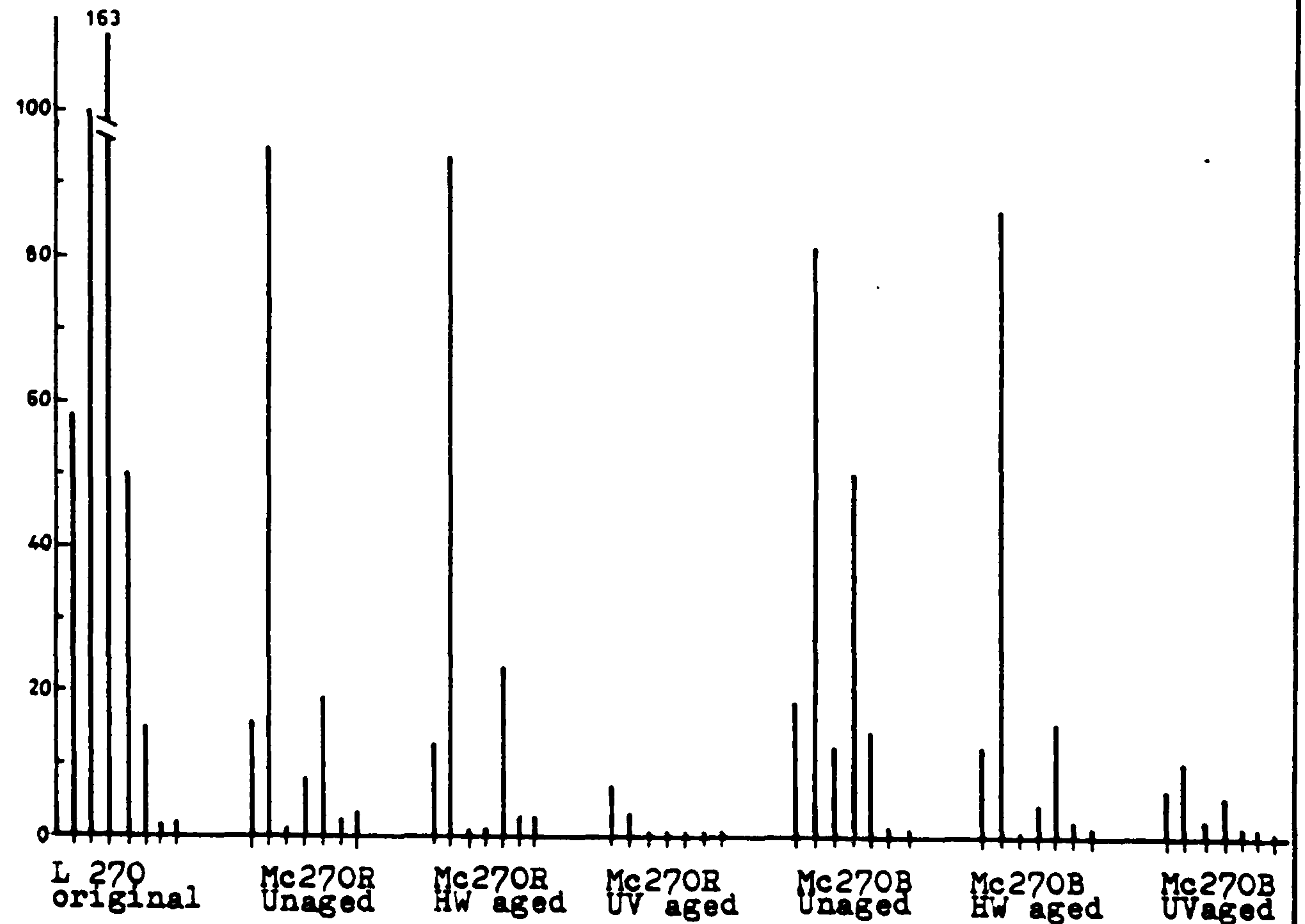

Figure 22 L.C. Comparative profiles of Loctite 270 major constituents.

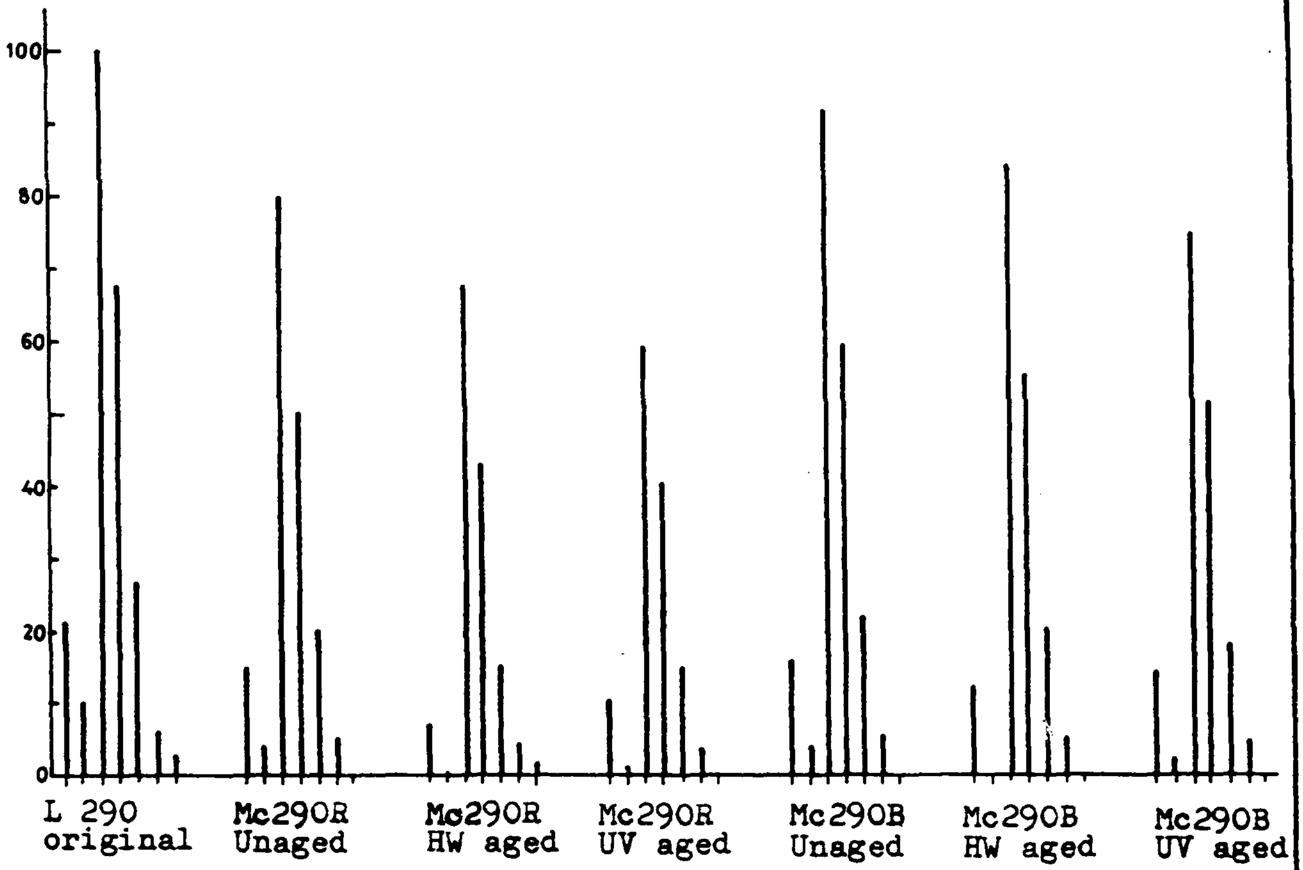

Figure 23 L.C. Comparative profiles of Loctite 290 additives.

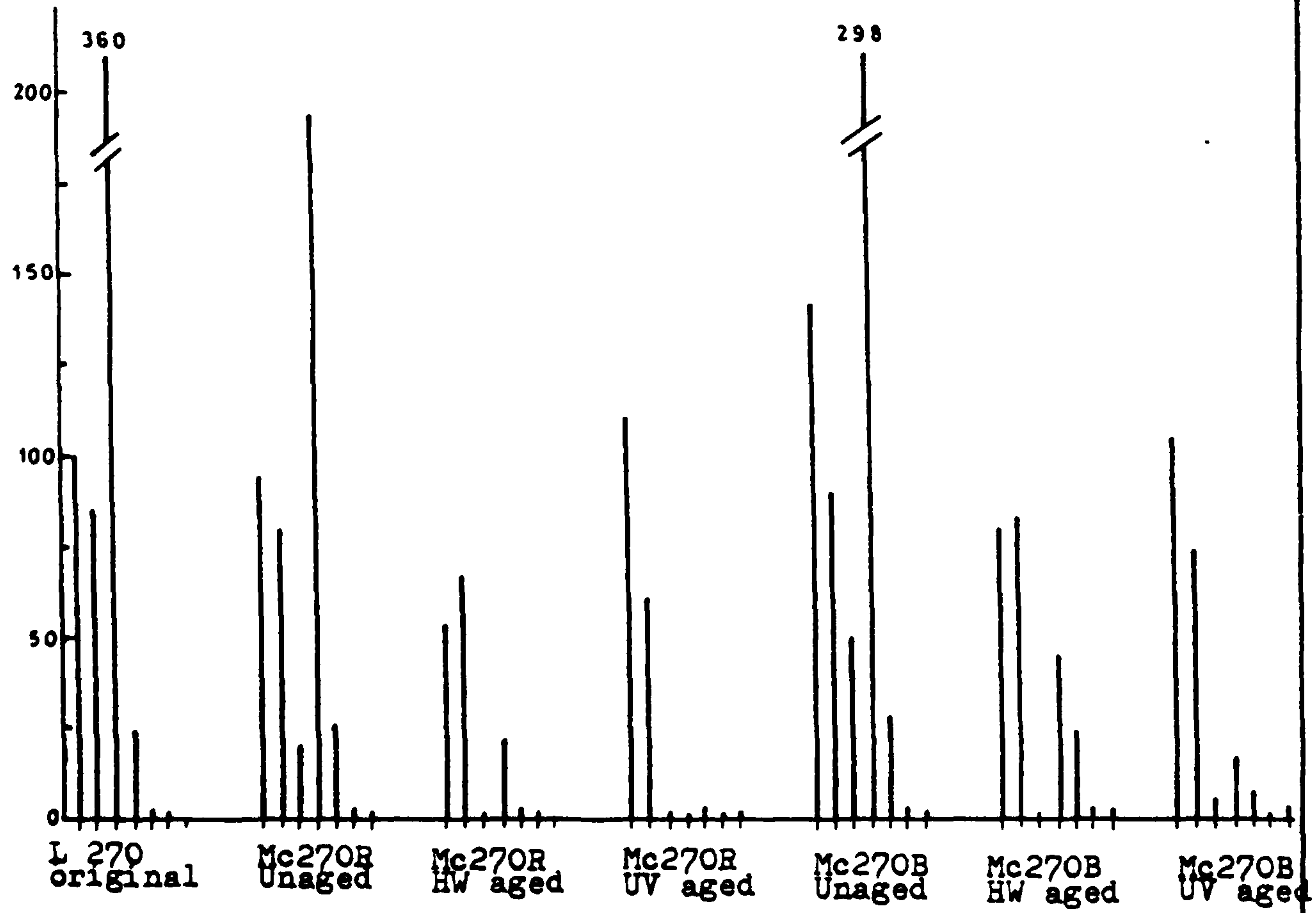

Figure 24 L.C. Comparative profiles of Loctite 270 additives.

5 - Characterization of epoxy resins by liquid chromatography. Stability studies.

As disclosed in previous Report, the epoxy resin Bepox LX/21 chosen for conducting the microencapsulation studies is a low viscosity liquid resin, based on DGEBA, which contains cresyl glycidyl ether as reactive diluent

By following the same "philosophy" as for anaerobic systems, chromatographic analysis have been conducted on Bepox resin in order to asses its composition which serves as reference for stability evaluations on both unencapsulated and encapsulated form.

For characterizing the original resin, gel permeation chromatography (GPC) was used.

A kit with four columns of μ-styragel: 500 - 500 - 100 - 100 Å was used, with tetrahydrofurane (THF) as mobil phase (solvent) with a flow of 2 ml/min. UV detector at 254 nm has been used. The sample is injected dissolved in THF, with a concentration of 14.3 ml sample in 5 ml THF.

The GPC chromatogram obtained is presented in Figure 25. This chromatogram shows a good feature for control purposes, because peaks are well separated and there is no problem for a precise integration of major monomeric constituent.

In order to attain isolated constituents which might be used as standards for quantitative titrations, low pressure column chromatographic fractionations were conducted by using the same column as for anaerobic systems but different eluents. A portion of approx.

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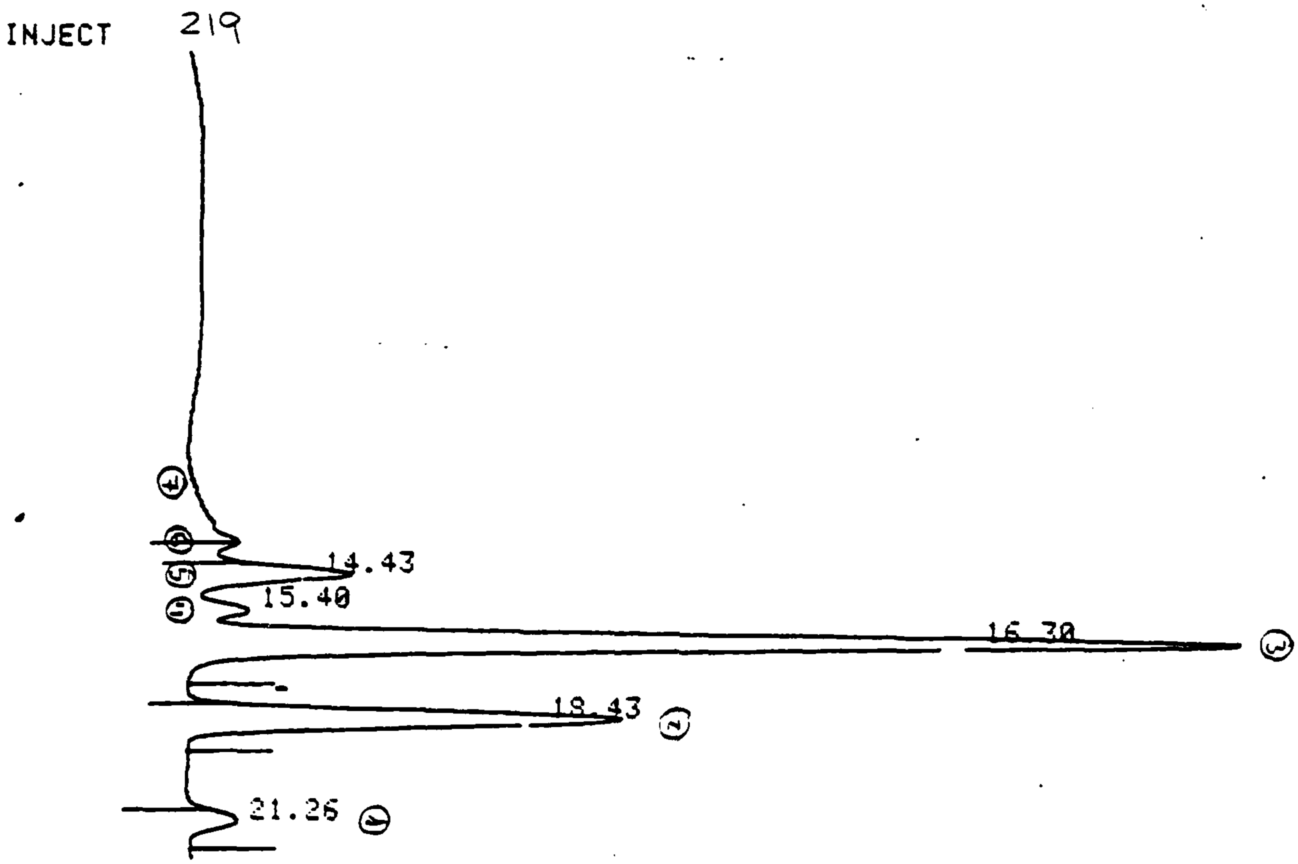

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                               CHART  0.50 CM/MIN
                               RUN #3                       CALC #0
COLUMN                         SOLVENT                   OPR ID:       5

EXTERNAL STANDARD QUANTITATION

 PEAK#             AMOUNT       RT      EXP RT      AREA              RF
                1662.16000     14.43              1662166 F     0.000000E0
                 430.43000     15.40               430430 F     0.000000E0
               13285.50000     16.30             13285607 L     0.000000E0
                5736.09000     18.43              5736116 L     0.000000E0
                 692.03400     21.26               692034 L     0.000000E0
TOTAL          21806.20000
```

Figure 25 - GPC chromatogram for epoxy resin (Bepox LX/21).

400 mg of resin dissolved in benzene was introduced into the column and several fractions were eluted by using benzene, ethyl ether, and isopropyl alcohol as eluotropic solvents. In all runs over 95% of sample weight were recovered.

A satisfactory separation between cresyl glycidyl ether (CGE) and DGEBA was achieved allowing quantitative determinations of both constituents. Another fraction of DGEBA containing OH groups was separated from the bulk DGEBA allowing the titration of that DGEBA polar.

By using the isolated pure CGE as external standard for chromatographic evaluations, the following composition has been estimated for Bepox LX/21 resin.

DGEBA (n = 0,1)	70% wt
DGEBA (with free OH)	8% wt
Cresyl glycidyl ether	22% wt

On the basis of the above study, the following peaks assignation can be done for Bepox GPC chromatogram.

Peak	Retention time (min)	Assignation
1	21.3	Total permeation limit.
2	18.4	Cresyl glycidyl ether.
3	16.3	DGEBA, n = o
4	15.4	DGEBA, n = o, with free OH
5	14.4	DGEBA, n = 1
6	13.5	DGEBA, n = 1, with free OH
7	13	DGEBA, n > 1

The standard or reference profile, for qualitative control or stability studies, is formed by the area ratios of peaks 2, 3, 4 and 5, taking as basis 100 the area of peak 3.

Quantitative evaluation of diluent (CGE) is obtained by direct titration using the external standard method, as described before.

In order to assess the stability for encapsulated Bepox resin, aliquots of a sample were subjected to ambient aging in the following environmental conditions:

		Code
a)	23ºC ± 2ºC, 50% RH ± 5% RH for one year	Mc Bepox SA
b)	40ºC ± 2ºC, 70% RH ± 5% RH during four months	Mc Bepox HW
c)	Exposed under ultraviolet light at 40ºC ± 2ºC, during 20 days	Mc Bepox UV

In Table XII are presented the chromatographic data obtained for capsules active contents extracted with tetrahydrofurane in an ultrasonic bath.

In that Table are included, in addition to the GPC profiles, the quantitative contents for cresyl glycidyl ether and DGEBA monomer (n = o), evaluated with external standards.

In Figure 26 can be viewed the chromatogram of a representative sample included in Table XII. In that Figure a band broadening can be observed in the oligomers zone. This band broadening appears in all chromatograms of aged capsular Bepox, indicating the presence of species with higher molecular weight in aged capsules with regard to the initial composition.

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It is interesting to note the increase experimented by peak 4 in Mc Bepox HW sample. This peak previously assigned to DGEBA n = o with free OH, effectively increase in moist ambient, where hydrolysis is favoured, supporting thus the assignation given.

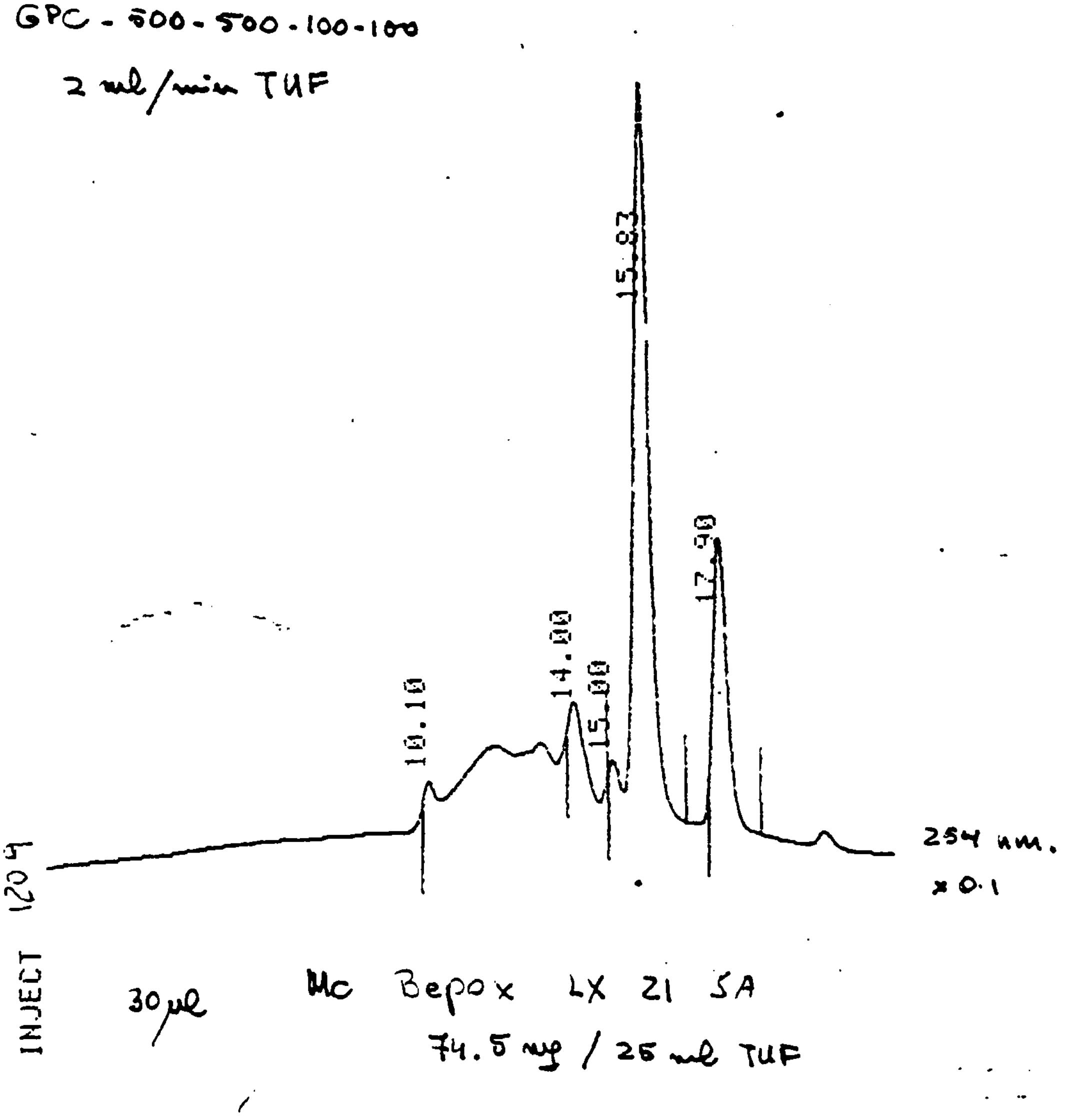

Figure 26 - GPC chromatogram for encapsulated Bepox LX/21 resin, aged during one year at 23ºC ± 2ºC, 50% ± 5% RH.

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TABLE XII - GPC EVALUATION OF AGED BEPOX LX/21 CAPSULES

Sample Code	Chromatographic profiles (Peaks) (2)	(3)	(4)	(5)	Diluent contents (CGE) %	DGEBA (n=o) Contents	Oligomers Contents (DGEBA n >1)
epox LX/21 riginal resin	43	100	4	13	22	Co	1% of total area
lc Bepox SA	40	100	2	9	11.5	0.55 Co	30% " " "
lc Bepox HW	2	100	10	9	0.7	0.56 Co	41% " " "
lc Bepox UV	0	100	--	10	traces	0.09 Co	55% " " "

SECTION III

CONCLUSIONS

Microencapsulation improvements.

Additional microencapsulation trials have been conducted on both, anaerobic compositions and epoxy resins in order to achieve capsular products with higher active core contents and/or better stability.

In the case of anaerobic compositions, with a carefully control during the agitation step and by using a mechanical stirrer specifically designed to provide an even dispersing action with low rotation speeds (below 300 rpm), stable capsules with active contents ranging from 82.5% to 93% were achieved representing a significative enhancement in comparison with previous trials in which capsules with active contents varying from 72% to 88% were obtained.

For epoxy resins, the effect of resin temperature proved be significant. Within the same experimental procedures by increasing the resin temperature from 20ºC to 40ºC, both the capsules size distributions and average size were reduced to less than a half in most cases.

The effect of some resin additives on epoxy capsule properties was studied. Triethanolamine was the only additive that gave benefitial results, since when using that chemical in very low ratios (ranging from 0.1 up to 1.0 parts per cent), capsules with high active contents (approx. 90%) and satisfactory long term stability (over 18 months) were obtained.

Attempts conducted for development of capsular epoxy formulations with improved homogeneity by anchoring the hardener on the capsule surfaces, did not give satisfactory long term stability because some hardener's penetration through the shell was always produced in the coating stage, leading to a progressive capsules hardening.

Capsular adhesives stability.

Studies for determining capsular systems stability have been conducted under various environmental conditions.

The stability of encapsulated anaerobic systems (Loctite 270 and Loctite 290) extends over 10 months when stored under standard ambient conditions. Stability for these systems is markedly reduced when maintained at temperatures above the ambient. Thus, capsular shelf life when stored at 40ºC is limited to 4 - 6 months. Capsular Loctite systems are also highly susceptible to ultraviolet light, suffering a substantial hardening in short time. Loctite 290 capsules are more sensitive to UV radiations than Loctite 270.

The stability of the Bepox LX/21 capsules extended over 18 months when stored under standard ambient conditions. These capsules are not affected by light and shows also a noticeable stability to UV light, since samples exposed to these radiations for up to 20 days in an accelerated UV aging chamber, did remain still active.

Capsular formulations of Bepox/HT 972, are stable over one year when stored at temperatures below 25ºC and with relative humidity ranges from 40% up to 70%. For high relative humidity these formulations tend to become

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lumpy. This fact nevertheless does not affect its bonding characteristics.

Bonding properties of capsular systems.

Lap shear tests have been conducted for assessing the bonding properties of unaged and aged capsular adhesives.

Lap shear values for unaged capsular anaerobic adhesives are about 75% to 80% with regard to the lap shear strengths for the original unencapsulated systems.

Adhesion tests on aged capsular anaerobic systems confirm the previous results determining the stability limits for these adhesives. Thus, no significative changes in lap shear strengths were noticed upon testing capsular Loctite's samples kept in standard laboratory ambient for ten months before test.

When dealing with capsular epoxy adhesives, typical lap shear values for unaged samples are in the range of 80 to 85% with regard to the lap shear strengths for the original unencapsulated systems. Excellent bonding properties are retained in samples stored up to 18 months under standard laboratory ambient.

On the contrary, samples stored at 40ºC/85% RH show an unstable performance since an initial improvement in shear strength is clearly noted but, after a short time, adhesion strength fails sharply below 30% of the initial value.

For the epoxy systems used in this Project, similar storage stability is achieved for capsular adhesives

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when each constituent (hardener and encapsulated resin) are stored separately, than if both constituents are previously dry mixed and the resulting formulation is stored as "one can" adhesive.

Capsular adhesives characterization by liquid chromatography. Ageing monitoring.

Liquid chromatographic techniques have been extensively used for characterizing raw materials, as well as encapsulated systems.

Low pressure column chromatography has proved to be a powerful tool for fractionation of complex compositions and for isolating individual constituents.

HPLC and GPC have proved their capability not only as analytical tool, but also for monitoring the chemical changes associated to ageing processes, allowing thus a complementary evaluation of the capsular adhesives stability. The results achieved within this task are in good agreement with those previously disclosed.

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