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Prompt Non-Tire Rubber Recycling: Final Report for Phases 1 and 2

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Prompt Non-Tire Rubber Recycling: Final Report for Phases 1 and 2

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Notation

The following is a list of acronyms, initialisms, and abbreviations (including units of measure) used in this document.

ARDL — Akron Rubber Development Laboratory

CRP — Catalytic Regeneration Process

DPG — N,N'-diphenylguanidine

DPTH — dipentamethylenethiuram hexasulfide

DTDM — 4,4-dithiodimorpholine

EPDM — ethylene-propylene-nonconjugated-diene monomer

ETA — Environmental Technologies Alternatives, Inc.

EPA — Environmental Protection Agency

FTIR — Fourier transform infrared analysis

GPC — gas-phase chromatography

MBTS — 2-benzthiazolyl disulfide

NBR — nitrile butyl rubber

Neoprene — polychloroprene

NR — natural rubber

OSHA — Occupational Safety and Health Administration

phr — parts per hundred rubber

quad — quadrillion (10^{15}) Btu

SBR — styrene-butadiene rubber

SMR — standardized Malaysian rubber

STMC — Scrap Tire Management Council

TMTD — tetramethyl thiuram disulfide

TMTM — tetramethyl thiuram monosulfide

UDT — Ultrasonic Devulcanization Technology

ZBDC — zinc dibenzyl dithiocarbamate

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ACM, Inc.	Rick Moore, President

Abstract

This report summarizes an assessment conducted by Environmental Technologies Alternatives, Inc., under a subcontract to Argonne National Laboratory. The project was conducted in two phases. An assessment of alternative technologies for recycling of prompt non-tire rubber was conducted in the first phase, and an experimental program focusing on a new technology called the Catalytic Regeneration Process was conducted in the second phase. The assessment of alternative emerging technologies indicated that the Catalytic Regeneration Process offered the greatest opportunity for recovery of high-value recyclable rubber material. An experimental and large-scale test program was undertaken to further delineate the economic potential as an essential step leading to commercial deployment and to determine the course of continued development of the technology by the private sector. The experimental program defined process-operating conditions for the technology and verified the degree of devulcanization achievable for two rubber compounds: ethylene-propylene-nonconjugated-diene monomer (EPDM) and neoprene. To determine product acceptance, samples of devulcanized EPDM and neoprene were prepared and used in factory trials for the production of automotive moldings (EPDM) and fiber-filled belting (neoprene). The factory trials indicated that the physical properties of the products were acceptable in both cases. The appearance of molded and calendared surface finishes was acceptable, while that of extruded finishes was unsatisfactory. The fiber-filled neoprene belting application offers the greatest economic potential. Process costs were estimated at $0.34/lb for neoprene waste rubber relative to a value of $0.57/lb. The results of the experimental program led to the decision to continue development of this technology within the private sector. A pilot-scale demonstration for this technology is being planned, subject to the availability of about $3 million in financing from private-sector investors. The ability to recycle non-tire rubber scrap could conserve as much as 90,000 Btu/lb, thus yielding an estimated energy savings potential of about 0.25 quad/yr.

Executive Summary

In 1993, the U.S. consumption of rubber (elastomers) was about 3.0×10^9 kg. Non-tire rubber applications accounted for about 40% of this consumption. Currently, a negligible percentage of non-tire rubber is recycled. The ability to recycle non-tire rubber scrap could conserve as much as 90,000 Btu/lb, thus yielding an estimated energy savings potential of about 0.25 quad/yr. This report summarizes an assessment conducted by Environmental Technologies Alternatives, Inc., under a subcontract to Argonne National Laboratory. The project was conducted in two phases. An assessment of alternative technologies was conducted in Phase 1, and an experimental program focusing on the Catalytic Regeneration Process (CRP) technology was conducted in Phase 2.

Phase 1 of this project consisted of examining a number of emerging non-tire rubber recycling technologies. This initial screening included an in-depth interview, after which six technology developers were offered the opportunity to participate in a first-stage assessment that would comparatively evaluate the physical properties of recompounded rubber by using scrap rubber processed by each technology. Three of the technology developers elected to participate and used one of the following technologies: peel-grind/cryogenic system, CRP, and ultrasonic devulcanization technology (UDT). Of these, both the UDT and the CRP technologies provided some level of devulcanization of the scrap rubber, unlike the granulation offered by the peel-grind technology. Thus, these two technologies would be expected to have a broader market potential. The material properties of the CRP-processed rubber were much closer to the properties of the original compound than were the properties of the UDT-processed rubber. For example, in aged condition, the tensile strengths of the UDT and CRP processed material were, respectively, 39% and 88% of the original ethylene-propylene-nonconjugated-diene (EPDM) monomer. In addition, there are many uncertainties associated with the design, development, and manufacturing of large-scale UDT equipment. By comparison, the CRP uses proven, off-the-shelf equipment. Therefore, during Phase 2 of the project, the focus was to determine the performance capabilities of the CRP technology.

The CRP, a rubber devulcanization process, was developed by Relastomer USA. In this patented process, the size-reduced scrap rubber is swelled by using appropriate solvents, and the resultant slurry is pumped through a series of catalytic screens. The breakdown of carbon-sulfur bonds is accelerated in the presence of a suitable metal catalyst, such as copper, cobalt, and manganese. The screens also serve to reduce the size of the devulcanized scrap rubber. The solvent is recovered, and the moisture in the devulcanized rubber material is removed.

An experimental and large-scale test program was undertaken to further delineate the economic potential of the CRP as an essential step leading to commercial deployment and to determine the course of continued development of the technology by the private sector. The experimental program defined the process operating conditions for the technology. This program also verified the degree of devulcanization achievable for two rubber compounds: EPDM and neoprene. To determine product acceptance, samples of devulcanized EPDM and neoprene were prepared and used in factory trials for the production of automotive moldings (EPDM) and fiber-filled belting (neoprene). The factory trials indicated that the physical properties of the products were acceptable in both cases. The appearance of molded and calendared surface finishes was acceptable, while that of extruded finishes was unsatisfactory. The fiber-filled neoprene belting application offers the greatest economic potential. Process costs were estimated at $0.35/lb for neoprene waste rubber relative to a value of $0.55 to $0.60/lb for the devulcanized scrap material. The results of the experimental program led to the decision to continue development of this technology within the private sector. A pilot-scale demonstration for this technology is being planned, subject to the availability of about $3 million of financing from private-sector investors.

Section 1
Introduction

In 1993, total U.S. consumption of rubber (elastomers) was about 3.0×10^9 kg (SRI International 1995). Of this total, consumption of natural rubber (NR) represented one-third and consumption of synthetic rubber represented the remaining two-thirds. In 1995, about 81% of natural rubber was used in tire-related applications (SRI International 1996). Synthetic rubber is of two types: general purpose and specialty (Smith et al. 1995). General purpose synthetic rubber constitutes the bulk of synthetic rubber consumption, and about 50% of general purpose synthetic rubber is used by tire manufacturers. Non-tire applications include a wide variety of products, such as rubber footwear; automotive rubber hoses, belts, and engine mounts; rubber seals; rubberized fabrics; vulcanized rubber clothing; rubber-based medical and health-related supplies; and custom-made rubber products.

The Scrap Tire Management Council (STMC) estimates that the market demand for scrap tires reached a record 174.5 million tires, or about 69% of the 253 million scrap tires generated in 1995. These scrap tires were used in many applications: 130 million scrap tires were burned as tire-derived fuel (Scrap Tire News 1996a). In contrast, a negligible percent of non-tire rubber is currently recycled. The total energy savings potential attributable to recycling of non-tire rubber is estimated to be about 0.25 quad/yr.

Although considerable research has focused on the recyclability of tire rubber, relatively little research has addressed the recyclability of non-tire rubber elastomers, which have different chemistries than tire rubber. This report summarizes the results of a two-phase project undertaken to determine the technical and economic feasibility of prompt non-tire rubber recycling. The first phase was an assessment of alternative technologies, and the second phase was an experimental program to evaluate the technical and economic potential of a specific technology.

Section 2
Review of Emerging Non-Tire Rubber Recycling Technologies

2.1 Phase 1 Overview

In Phase 1, nine non-tire rubber recycling technologies/candidates were identified:

- Solid-state shear extrusion — Illinois Institute of Technology
- Double rotor hammermill — Polytech Recycling Corporation
- Ambient grinding innovation — Arden Just
- Stearic treatment of rubber particles — Eurathane Technologies
- Solid-state shear extrusion — Northwestern University
- Ultrasonic devulcanization technology (UDT) — Akron University and National Feedscrew and Machining Industries, Inc.
- Catalytic Regeneration Process (CRP) — Relastomer S.A.
- Peel-Grind /Cryogenic System — Lagrone Technical Consulting
- DeLink/DeVulc — STI-K Polymers

Phase 1 of the program focused on the preliminary screening of these nine technologies. The screening consisted of an in-depth interview with the technology developer and an on-site visit at the trial facility, when considered appropriate. Six of the nine technology developers were asked to participate in a first-stage assessment, which would include preparation of processed scrap rubber for a comparative evaluation of the physical properties of recompounded rubber, relative to virgin compounds. Only three technology developers chose to participate. The technologies that were then evaluated were as follows:

- Peel-Grind/Cryogenic System
- CRP
- UDT

Trial evaluations of these three technologies were initiated. Two widely used recipes were chosen as control recipes for comparing properties of original and recycled rubbers. Table 2.1 provides a typical natural-rubber recipe for producing a general-purpose engine mount and a

Table 2.1 Standard Formulations of NR and EPDM Compounds

Ingredient	NR Compound (phr)	EPDM Compound (phr)
N550 black	45.00	200.00
Zinc oxide	5.00	5.00
Stearic acid	2.00	1.00
Sulfur	2.25	0.50
SMR	100.00	
Light oil	10.00	
Antioxidant	2.00	
Antiozonant	2.00	
MBTS	1.00	
DPG	0.20	
DTDM	1.00	
Epsyn 5508		70.00
Epsyn 70A		30.00
Circusol 4240		140.00
Paraffin Wax		5.00
TMTD		1.50
TMTM		1.50
DPTH		1.00
ZBDC		1.50
Total	170.45	457.00

typical EPDM recipe for producing radiator heater hose. The following sections provide a summary of each evaluation.

2.2 Testing and Evaluation of Peel-Grind/Cryogenic System

This technology is a new fine-cryogenic grinding process offered by Lagrone Technical Consulting, Inc., Vicksburg, Miss. The proprietary equipment enables processing at or near the embrittlement temperature of the material being processed. This process can be retrofitted to old or new impact pulverizers at a minimal cost. Performance evaluation trials on this technology were conducted on January 10 and 11, 1996. However, the trials failed to confirm the earlier results because of a series of processing deficiencies related to nitrogen supply and mechanical parts failure. The overall processing improvements achieved under the best performance were, at best, only small incremental improvements over existing cryogenic processing.

2.3 Testing and Evaluation of UDT

The UDT process was invented by Isayev and Chen (Isayev 1993; Isayev and Chen 1994) at the University of Akron. In this process, small particles of rubber are exposed to ultrasonic energy under controlled temperature and pressure operating conditions (Scrap Tire News 1996b). The UDT process was evaluated with trial runs on NR and EPDM compounds. The properties of devulcanized rubber were compared with those of original compounds by Akron Rubber Development Laboratory (ARDL). To prepare cured samples for testing, additional amounts of curatives were added to the devulcanized materials in a Banbury mixer. The amount and type of curatives added are presented in Table 2.2. Tables 2.3 and 2.4 present a comparison of properties for the NR and EPDM trials, respectively.

In the case of NR and EPDM unaged compounds, the devulcanized compound had only about 24% and 23%, respectively, of original tensile strength and 43% and 20%, respectively, of original elongation. In the case of NR- and EPDM-aged compounds, the devulcanized compound had only about 35% and 39%, respectively, of original tensile strength and 48% and 25%, respectively, of original elongation. The tear strength was about 32% of the original value for devulcanized NR and 31% of that for devulcanized EPDM.

Table 2.2 Amount of Curatives Added to Devulcanized Rubber from UDT Process

Ingredient	NR Sample (phr)	EPDM Sample (phr)
Original compound	170.45[a]	457.00[b]
Sulfur	1.00	0.12
MBTS	0.25	
Sulfasan R	0.25	
TMTD		0.40
DPTH		0.12
Total	171.95	457.64

[a] See column 2 in Table 2.1.

[b] See column 3 in Table 2.1.

Table 2.3 Selected Properties of NR and Rubber Processed by UDT and CRP Technologies

Property	Natural Rubber	UDT Processed Rubber	CRP Processed Rubber
Specific gravity	1.107	1.123	1.140
Unaged condition:			
100% modulus (psi)	530	350	560
Elongation at break (%)	510	220	120
Tensile strength (psi)	4275	1020	800
Hardness (shore A)	63	53	63
Aged condition:			
100% modulus (psi)	530	440	520
Elongation at break (%)	440	210	170
Tensile strength (psi)	3330	1150	1010
Hardness (shore A)	63	65	66
Tear strength (die B; ppi)	678	220	157
Compression set (%)	24.8	30.2	28.5

Table 2.4 Selected Properties of EPDM and Rubber Processed by UDT and CRP Technologies

Property	EPDM	UDT Processed Rubber	CRP Processed Rubber
Specific gravity	1.178	1.201	1.150
Unaged condition:			
100% modulus (psi)	350	250	870
Elongation at break (%)	660	130	120
Tensile strength (psi)	1235	290	1050
Hardness (shore A)	65	51	67
Aged condition:			
100% modulus (psi)	465	410	1110
Elongation at break (%)	475	120	90
Tensile strength (psi)	1170	460	1030
Hardness (shore A)	74	59	74
Tear strength (die B; psi)	290	91	80
Compression set (%)	24.2	47.9	31.4

2.4 Testing and Evaluation of CRP

The CRP technology was developed by Valverde (1996). In this patented process, the size-reduced scrap rubber is swelled by using appropriate solvents, and the resultant slurry is pumped through a series of catalytic screens. The breakdown of carbon-sulfur bonds is accelerated in the presence of a suitable metal catalyst, such as copper, cobalt, or manganese. These screens also serve to reduce the size of the devulcanized scrap rubber. The solvent is recovered, and the moisture in the devulcanized rubber material is removed.

To prepare samples for testing, devulcanized dry powder was converted to sheet form on a 6-in. two-roll mill. In accordance with the instructions of the processor, 75% of curing agents in the original recipe (Table 2.1) were added to compensate for losses in curing agents that occur during the devulcanization process. Table 2.5 provides a list of the added ingredients.

Table 2.3 shows the selected properties of ground original NR and devulcanized rubber with the CRP process. Table 2.4 details the selected properties of ground original EPDM and devulcanized rubber with the CRP process. The devulcanized rubber is produced in a very fine particle size (2–25 μm). For both aged and unaged compounds, based on 100% devulcanized EPDM material, the tensile strength was about 90% of that of the original EPDM. However, for aged and unaged compounds, based on 100% devulcanized NR, the tensile strength was about 30% and 20%, respectively, of that of the original NR compound.

Table 2.5 Amount of Curatives Added to Devulcanized Rubber from CRP

Ingredient	NR Sample (phr)	EPDM Sample (phr)
Original compound	170.45[a]	457.00[b]
Zinc oxide	3.75	3.75
Stearic acid	1.50	0.75
Sulfur	1.69	0.38
MBTS	0.75	
DPG	0.15	
DTDM	0.75	
TMTD		1.12
TMTM		1.12
DPTH		0.75
ZBDC		1.12
Total	179.04	465.99

[a] See column 2 in Table 2.1.

[b] See column 3 in Table 2.1.

An evaluation was also made for EPDM material containing 35% devulcanized EPDM rubber. This material (in aged condition) had 84% of the tensile strength found in the original EPDM material. The effect of the solvent on EPDM devulcanized rubber was also studied. It appeared that more vulcanization occurred in hexane than in toluene. The tensile strength for hexane-based EPDM devulcanized rubber was 11% higher than that for the toluene-based rubber.

2.5 Phase 1 Conclusions

In general, the physical properties of the CRP-processed scrap rubber were better than those of the UDT-processed scrap rubber. Estimating the cost of reliable critical ultrasonic equipment that would be required for high-volume production at this time cannot be done with any degree of confidence. Too many uncertainties exist with regard to the design, development, and manufacture of the equipment. By comparison, the CRP technology uses proven off-the-shelf equipment for high-volume scale-up. The most critical element of the CRP technology, the metal catalytic reactor, had already been scaled up and was operational at the time of evaluation. Therefore, Phase 2 of this project focused on the CRP technology.

Section 3
Technical and Economic Evaluation of the Catalytic Regeneration Process

3.1 Phase 2 Overview

The objective of Phase 2 was to determine the course of continued development of the CRP by the private sector. The ultimate decision was to proceed with the development of this technology.

This patented technology (Lima 1997) was developed by Relastomer S.A. (Baranwal et al. 1998) The basic process concept is shown in Figure 3.1. The feed material is ground to particle size, ranging from 2 to 40 μm. The rubber is swelled by using appropriate solvents to form a dense slurry, which is pumped through a series of catalytic screens. The breakdown of carbon-sulfur bonds (devulcanization) is accelerated in the presence of a suitable metal catalyst, such as copper, cobalt, or manganese. The function of the metallic catalytic screens is twofold. The screens slice and dice the soft, swollen rubber particles, and the catalytic metals break the chemical crosslinks in the vulcanized scrap rubber. When the resultant devulcanized rubber particulate is dried, it shrinks by the same factor by which it had swelled, yielding a very fine devulcanized rubber particulate for reuse. The solvent is recovered and the moisture in the devulcanized rubber material is removed.

In order to reach a decision regarding continued development of the CRP by the private sector, the following tasks were conducted: (1) bench-scale research to determine the most suitable solvents for use in processing of scrap rubber, followed by extensive bench-scale devulcanization experiments; (2) large-scale compounding and molding (reuse) trials using devulcanized material processed by CRP; and (3) estimation of process economics.

3.2 Bench-Scale Research

Bench-scale research was conducted to identify the preferred solvents for certain rubber compounds, to determine the preferred CRP operating conditions and performance, and to characterize the regenerated/devulcanized rubber from the CRP.

3.2.1 Solvent Selection

The criteria for selection of the two most suitable solvents for a wide range of non-tire polymer compounds are listed below.

The solvents must:

- Be environmentally acceptable and capable of safe and easy handling during the process;
- Be compatible with the polymers to be recovered;

- Be readily available at a reasonable price;
- Have boiling points lower than 85°C, which is the process drying temperature;
- Have an acceptable swelling rate/process time; and
- Have greater than a 99% solvent recovery rate.

On the basis of these criteria, nine solvents were evaluated. After evaluating these solvents, the following choices were made: cyclohexane for processing of EPDM and ethyl acetate for processing of neoprene. The laboratory analysis and recommendations to support these choices are detailed in Appendix A.

3.2.2 Processing Conditions

After considering previous laboratory trials and accumulated data, the catalytic components for each prompt waste feed stock were selected on the basis of the following considerations:

- Original compound properties;
- Particle size of the particulate waste feed stock;
- Percent of residual fiber, if any, in the feed stock;
- Optimum swelling reaction time of the particles;
- Relative softness of the swollen particulate;
- Restriction limits versus pumping pressures at each reactor phase of the process;
- Selected number of passes required to achieve optimum processing; and
- Desired final processed particle size.

For neoprene with ethyl acetate as the solvent, five reactor passes, with a slightly larger particle size to accommodate fiber processing by the reactor, were selected. For EPDM and cyclohexane as the solvent, a ratio of 7 solvent to 1 polymer was selected, along with five reactor passes.

3.2.3 CRP Material Characterization

In considering the potential of CRP technology, it was determined that the application of this process with some specialty rubber should be examined, since more cost incentives would be associated with specialty rubbers than with general purpose types of rubbers. To that end, extensive laboratory testing of the CRP-processed neoprene and EPDM scrap rubber was done. The tests are detailed in Appendix B.

The results of the extensive laboratory testing revealed the following:

- The crosslinking density and subsequent calculations of the degrees of devulcanization indicate that devulcanization occurs and tends to increase with increased processing time and/or cycles.

- The densities of the CRP samples were less than those of the unprocessed scrap rubber. This result was unexpected; no explanation can be offered because there does not appear to be any significant loss of additives and curatives.

- The recovered ethyl acetate solvates the scrap rubber as well as fresh ethyl acetate, indicating that no changes occur to the solvent during swelling, evaporation, and recovery. Thus, solvent can be recycled in the process.

- Analyses of the solvent residues indicate that no polymer or oxygen-containing polymer fragments were present. Testing of these residues, however, indicated that dioctylated diphenylamine and paraphenylene diamine antidegradant species were present in small quantities. The analyses also indicated that no accelerator or curative fragments were present in these residues.

- Ro-Tap sieve analysis indicated that the particle size of the product decreased with increasing numbers of processing steps.

- Photomicrography of the neoprene CRP material confirmed that smaller particle sizes result from increasing numbers of processing steps, and "as-received" samples displayed some tendency to agglomerate.

- Microscopy indicated that there was no free carbon black in the CRP processed material, indicating that no polymer-carbon black bonds were broken during the processing.

The following are suggested mechanisms that might be causing devulcanization and/or size reduction.

Devulcanization. In the case of sulfur-modified neoprene, such as the G-type neoprenes, the polysulfidic crosslinks are susceptible to breakage (low bond dissociation energy, depending upon the number of sulfur atoms in the chain, -34 kcal/mol for $-C-S_4-C-$). Perhaps some breakage of sulfur-sulfur bonds also generates species that account for some of the observed regenerated reactivity. However, to break chemical bonds, significant energy input is required, and, as this process is run at room temperature, there is probably too little energy in the system to accomplish this.

With regard to polymer breakdown and catalytic activity, some of the transition metal elements (such as manganese, iron, cobalt, nickel, and copper) are known to catalyze the oxidation of natural rubber, and they could possibly have a similar effect on neoprene. However, the gas-phase chromatography (GPC) and Fourier transform infrared analysis

(FTIR) studies conducted by ARDL detected no aldehydic, carboxylic, or ketonic species. Neoprene is a high-gel polymer that is extremely hard to test for molecular weight. It was assumed that if catalyzed oxidation occurred, then lower-molecular-weight fragments would be present; they would be soluble and detectable, and their molecular weights could be determined. This was not the case. If catalytic oxidation is occurring in the neoprene, the generated species with the oxygen-containing functional groups must also be gels (or on the outer surfaces of the neoprene gel particles) that are not readily soluble.

In neoprene, the chlorine atoms and their molecular locations determine the reactivity of the polymer and, as neoprene is about 35% chlorine by weight, there are many chlorine atoms. We assume that the labile chlorines (tertiary allylic species) comprise around 1.6% of the virgin polymer, and these most reactive species are consumed during the initial curing. Other, less reactive (but nonetheless reactive) species are also present in neoprene: allylic, tertiary, and vinyl chlorines that, if not consumed during cure, might still be available for subsequent reactions. Some rearrangement of chlorines could occur in the presence of certain materials to yield more reactive species, and perhaps this is what is occurring. It could be that the solvent swelling of the neoprene might permit some degree of polymer chain mobility and freedom for such rearrangements to occur.

***Size Reduction/Particle Fracture*.** Swelling in a suitable solvent for extended periods increases the size of the swollen rubber compound particles 4- to 7-fold. As these particles are pumped through such restrictions as metallic screens, the softened, swollen particles are sliced and diced repeatedly. As the restrictions become smaller, the swollen particles continue to be reduced in size. Upon drying, the sizes of the particles shrink 5- to 7-fold as the solvent evaporates. Considerable polymer fracture occurs as the swollen particles are passed through the screens. Because particle size is controlled by screen size, the use of very fine screens (200–400 mesh) will yield products with extremely fine particle sizes (as fine as 1–10 μm when dried).

3.3 Compounding and Molding Trials

CRP-regenerated neoprene scrap was tested by Dayco Co. in four trial runs of the following compound formulations: hose cover stock, non-fiber-filled V-Belt compression stock, and two formulations of fiber-filled V-Belt compression stock. In these evaluations, virgin neoprene was blended with two levels of CRP material — approximately 10 and 20 phr. Loadings of carbon black and fiber (where applicable) were also adjusted. No additional oil or curatives were added in these studies. Laboratory testing indicated comparable physical properties (tensile, elongation, modulus, and hardness) with the lower replacement ratio. At the higher ratio, slight deterioration of the physical properties was noted.

On several samples that were extruded in the laboratory, Dayco also noted that the regenerated material produced extrudates with much rougher textures. This may relate to the tendency of the regenerated material to agglomerate during packing and storage. While this poses no major problem for many compounds, it could be a serious detriment for compounds that are extruded, such as hose compounds. Additional studies will be required to more clearly understand and overcome this agglomeration tendency.

Two formulations of scrap rubber were processed by the CRP for use in these trials. These formulations were designated ETA-4, which refers to a non-fiber-filled scrap, and ETA-6, which refers to a fiber-filled scrap. In general, the performance of the reformulated compounds was not dependent on whether the source scrap material was fiber-filled, although some minor variations are noted (Baranwal et al. 1998). Each of the trials is discussed in the following sections.

3.3.1 Trial 1: Hose Cover Stock

In this study, both fiber-filled and non-fiber-filled derived CRP materials were used at 9.5 and 19.1 phr, respectively, in a proprietary neoprene hose cover stock. The test data are presented in Table 3.1.

In this trial, tensile strength and elongation decreased somewhat. Deterioration of properties upon aging was comparable. Cure rates were comparable in the two more modest substitutions and a little higher for the more aggressive replacements. Gehman low-temperature testing and compression set data were comparable. All of the dynamic properties were within 10% of the control values and roughly comparable. The addition of finely powdered CRP material to the compound resulted in an increase in viscosity and a decrease in scorch safety. While the experimental variations were adjusted for the carbon black (in the CRP material), no adjustments were made for additional processing oil or curatives.

3.3.2 Trial 2: Non-Fiber-Filled V-Belt Compression Stock

In this study, non-fiber-filled derived CRP material was used at 10 and 20 phr in a proprietary neoprene non-fiber-filled V-belt stock. The carbon black loading was adjusted, but the process oil and curatives loadings were not. The test data are presented in Table 3.2.

Again, some drop off occurred in tensile strength, with the modulus, elongation, and hardness properties being comparable with those of the control. Aged material properties were comparable with those of the control. Gehman low-temperature and compression set data were comparable. The cure rates were comparable. All the dynamic properties were within 10% of the control and were roughly comparable. The CRP-containing compounds again displayed higher compound viscosities and lower scorch safety. In this series, flex fatigue testing was done, and the CRP-containing compounds were inferior to the control.

3.3.3 Trial 3: Fiber-Filled V-Belt Compression Stock, Formulation A

In this study, both fiber-filled and non-fiber-filled derived CRP materials were used in a proprietary fiber-filled neoprene V-belt compression stock, replacing 5 and 10 phr of neoprene, respectively. Loadings of carbon black and fiber were adjusted, but no adjustments were made for processing oil or curatives. The test data are presented in Table 3.3.

Comparable tensile strengths could be seen with the ETA-6 CRP material, but some drop off occurred with the ETA-4 CRP material. There were some variations in the elongation data (higher with the ETA-6 CRP material, comparable with the ETA-4 CRP material) and modulus values (comparable with the ETA-6 CRP material, lower with the ETA-4 CRP material). These differences can be explained by the fact that the ETA-6 material contained fiber, which had been attrited and reduced during the processing, and the ETA-4 material contained no fiber. Hardnesses were comparable, as were the aged material properties. Cure rates and compression sets were comparable. Flex fatigue testing indicated improvements with the ETA-6 material. The dynamic properties were again within 10% of the control and roughly comparable. In this series, scorch times were comparable, and viscosities were up slightly with the 5-phr neoprene replacements and up even more with the 10-phr replacements.

Table 3.1 Physical and Dynamic Properties of Virgin and CRP Devulcanized Rubber: Trial 1. Hose Cover Stock

		Control				
Variation	Units	1	2	3	4	5
Polymer	PHR change	0	-3.8	-7.6	-3.8	-7.6
Carbon Black	PHR change	0	-2.9	-5.8	-2.9	-5.8
ETA-4	PHR change	0	9.5	19.1	0	0
ETA-6	PHR change	0	0	0	9.5	19.1
Physical Properties						
Tensile Strength	kPa	7,529	6,549	6,330	7,371	6,609
Aged Change	%	44	50	50	37	42
Elongation	%	206	191	172	208	208
Aged Change	%	-86	-86	-83	-87	-87
Shore A Durometer		82	83	85	83	84
Aged, Point Change		13	12	10	12	11
Modulus @ 100% Elong.	kPa	4,813	4,706	5,006	4,633	4,399
Cure Rate	N-m/min	0.308	0.287	0.371	0.286	0.324
MI 1 + 4 @ 100°C	N-m	10.40	10.509	14.35	10.96	11.87
Scorch @ 121°C	min	12.0	8.5	8.0	9.5	8.4
Gehman, T100	°C	-43	-43	-4.2	-43	-43
Compression Set	%	49	49	51	49	48
Dynamic Properties @ 12,000 cycles						
Loss Angle	degrees	13.02	12.7	12.95	12.68	12.72
Complex Modulus	kPa	34,702	34,150	37,922	36,275	34,172
Elastic Modulus	kPa	33,811	33,314	36,958	35,391	33,333
Inelastic Modulus	kPa	7,816	7,508	8,496	7,960	7,527

Table 3.2 Physical and Dynamic Properties of Virgin and CRP Devulcanized Rubber: Trial 2. Non-Fiber-Filled V-Belt Compression Stock

		Control		
Variation	Units	1	2	3
Polymer	PHR change	0	-4.1	-4.1
Carbon Black	PHR change	0	-3.1	-3.1
ETA-4	PHR change	0	10	20
Physical Properties				
Tensile Strength	kPa	16,052	15,459	14,162
Aged Change	%	-5.6	-4.6	-7.4
Elongation	%	241	243	228
Aged Change	%	-43.1	-42.7	-44.2
Shore A Durometer		82	82	80
Aged, Point Change		7	8	9
Modulus @ 100% Elong	kPa	6,268	6,019	5,647
Cure Rate	N-m/min	0.802	0.816	0.826
MI 1 + 4 @ 100°C	N-m	4.75	5.31	5.88
Scorch @ 121°C	min	2.6	4.7	6.0
Gehman, T100	°C	-42.25	-42.80	-42.15
Compression Set	%	36	36	36
Fatigue to Failure	Cycles	9,050	1,250	1,400
Dynamic Properties @ 12,000 Cycles				
Loss Angle	degrees	7.15	7.06	7.07
Complex Modulus	kPa	36,050	35,636	34,549
Elastic Modulus	kPa	35,796	35,391	34,311
Inelastic Modulus	kPa	4,489	4,385	4,257

3.3.4 Trial 4: Fiber-Filled V-Belt Compression Stock, Formulation B

In this study, the CRP materials replaced virgin neoprene at 5 and 10 phr in another proprietary fiber-filled neoprene V-belt stock. Loadings of carbon black and fiber were adjusted, but no adjustments were made for processing oil or curatives. The test data are presented in Table 3.4.

This study resulted in comparable modulus and hardness data, but some drop off occurred in tensile strength and elongation, particularly with the ETA-4 material. The cure rates were all comparable. Gehman and compression-set data were all comparable, with the exception of sample 5 on compression set. Flex fatigue testing indicated that all were comparable, with the exception of sample 2. All the dynamic properties were within 10% of the control and were roughly equivalent. Again, increases in compound viscosities and decreases in scorch safety were noted.

Table 3.3 Physical and Dynamic Properties of Virgin and CRP Devulcanized Rubber: Trial 3. Fiber-Filled V-Belt Compression Stock, Formulation A

		Control				
Variation	Units	1	2	3	4	5
Polymer	PHR change	0	-5	-10	-5	-10
Carbon Black	PHR change	0	-3.75	-7.5	-3.75	-7.5
Fiber	PHR change	0	-1.25	-2.5	0	0
ETA-4	PHR change	0	0	0	12.5	25
ETA-6	PHR change	0	12.5	25	0	0
Physical Properties						
Tensile Strength	kPa	11,120	11,377	11,087	10,556	9,853
Aged Change	%	-6	-11	-6	-7	-7
Elongation	%	310	351	355	321	311
Aged Change	%	-59	-54	-60	-59	-60
Shore A Durometer		85	85	83	84	83
Aged, Point Change		4	3	5	5	5
Modulus @ 100% Elong.	kPa	5,909	5,344	5,916	5,151	5,026
Cure Rate	N-m/min	1,580	1,580	1,664	1,607	1,535
MI 1 + 4 @ 100°C	N-m	7.80	8.70	9.72	8.25	8.81
Scorch @ 121°C	min	7.3	7.7	6.7	7.5	7.3
Compression Set	%	43	41	41	43	45
Fatigue to Failure	cycles	100	950	750	0	0
Dynamic Properties @ 12,000 Cycles						
Loss Angle	degrees	3.70	4.20	4.07	3.63	3.79
Complex Modulus	kPa	49,166	47,686	42,134	45,673	44,650
Elastic Modulus	kPa	49,063	47,558	42,027	45,581	44,552
Inelastic Modulus	kPa	3,174	3,495	2,994	2,893	2,951

3.3.5 Comments Regarding the Mold Tests

All tensile testing was done on a Monsanto T10 unit with an electronic data acquisition station by using methods based on ASTM 412, 3182, 3183, and 3676. Viscometric testing was based on ASTM 1646-96. Hardness testing was based on ASTM 2240. Aging was done in air for 70 h at 125° C. Gehman low-temperature testing was based on ASTM 832 and 1053. Compression sets were run for 22 h at 100°C and were based on ASTM 395, Method B. Fatigue-to-failure testing was done on samples aged for 48 h at 125°C and was based on ASTM 4482. Dynamic testing was done on a Dynamic Instron at 20 Hz in the compressive mode (10% pre-load deflection, +/- 5% articulation stroke), and data were collected at 6,000 and 12,000 cycles (only the 12,000-cycle data are presented in the tables). The compounding studies conducted by Dayco indicated that neither the ETA-4 nor the ETA-6 materials were "drop-in"

Table 3.4 Physical and Dynamic Properties of Virgin and CRP Devulcanized Rubber: Trial 4. Fiber-Filled V-Belt Compression Stock, Formulation B

		Control				
Variation	Units	1	2	3	4	5
Polymer	PHR change	0	-5	-10	-5	-10
Carbon Black	PHR change	0	-3.7	-7.5	-3.7	-7.5
Fiber	PHR change	0	-1.3	-2.5	0	0
ETA-4	PHR change	0	0	0	12.5	25
ETA-6	PHR change	0	12.5	25	0	0
Physical Properties						
Tensile Strength	kPa	9,232	8,791	8,371	7,722	6,516
Aged Change	%	-3	3	7	16	29
Elongation	%	547	557	510	436	412
Aged Change	%	-42	-41	-37	-46	-41
Shore A Durometer		75	73	73	73	74
Aged, Point Change		7	7	5	8	7
Modulus @ 100% Elong.	kPa	3,048	2,923	2,986	3,372	3,137
Tear @ Room Temp	kN/m	1,679	1,662	1,695	1,667	1,490
Cure Rate	N-m/min	0.620	0.623	0.626	0.671	0.668
MI 1 + 4 @ 100°C	N-m	6.55	7.91	9.94	9.27	9.72
Scorch T10 @ 121°C	min	6.70	6.10	4.90	5.50	4.90
Gehman, T100	°C	-42	-42	-42	-42	-42
Compression Set	%	35	35	38	37	40
Fatigue to Failure	cycles	3,350	1,500	2,850	3,450	2,350
Dynamic Properties @ 12,000 Cycles						
Loss Angle	degrees	5.48	5.43	5.17	5.17	5.66
Complex Modulus	kPa	29,733	27,924	25,481	28,166	27,950
Elastic Modulus	kPa	29,597	27,798	25,378	28,051	27,813
Inelastic Modulus	kPa	2,840	2,640	2,297	2,539	2,756

replacements for virgin neoprene in the four proprietary compounds in which they were tested. The materials were more similar to neoprene master batches, and their use would require adjustments for polymer, carbon black, fiber (if present), processing oil/plasticizer, and curatives. The physical properties were mostly consistent with those of 100% virgin polymer, excluding the increased viscosities, reduced scorch safeties, and the possible "dilution" effect on cure systems. Of particular note were the equivalencies demonstrated with the dynamic testing of the substitutions. For the most part, compression set and aged material data also indicated the viability of this approach. Further work, however, needs to be done to optimize the use of these materials.

3.4 Process Economics and Manufacturing Cost Estimate for CRP

On the basis of a market analysis of the potential for neoprene and nitrile prompt waste recovery, a plant capacity of 30 million lb/yr was selected. The plant would have two 15-million-lb/yr production lines, each independent, but both would operate under a lead operator and technician.

The net shippable output at a 75% operating efficiency and a 24-h, 5-day-per-week operation would be 22,500,000 lb annually.

The design criteria are as follows for each CRP line:

- 5 pumps at 75 hp each
    - 5 reactors plus replacements
    - twin holding tanks
    - centrifuge separation
    - drying and surface treatment
    - solvent recovery and handling system
    - general handling and packaging equipment
- A solvent recovery and drying system suitable for recycling the solvents and extracting solvents to the required 0.075% to 1% retention levels in the CRP materials.

The capital cost, including stock preparation for creating 30-mesh feedstock and the two CRP-processing lines, is estimated to be $3.5 million. The lines would be installed in two phases. Phase 1 would use feedstock preparation by subcontractors and would place line #1 into operation and properly refine it before installing line #2. Phase 2 would involve installing the necessary feedstock preparation facility to eliminate the cost of outside-purchased processing to 30 mesh.

The estimated total manufacturing cost, including direct and indirect costs for processing scrap rubber via the CRP technology, is $0.35/lb, as shown in Table 3.5. The estimated selling price of the CRP-processed material is $0.55 to $0.60/lb, yielding a margin of about 40%.

A breakdown of the direct CRP processing cost of $0.15/lb is shown in Table 3.6. The basis for the labor cost estimate is shown in Table 3.7. The estimated cost for size reduction of the rubber scrap to a 30-mesh-size feedstock to the CRP reactor is 0.25/lb, which is based on two-stage size reduction with removal of fibers and wires between stages.

Table 3.5 CRP Material Total Manufacturing Costs

Cost Component	Cost ($/lb)
Average freight in	0.025
Grinding to 30-mesh feed stock	0.125
Direct CRP processing costs	0.150
Subtotal/ direct mfg. cost	0.290
G&A @ 10%	0.029
Royalty payment	0.020
Total Manufacturing Cost	**0.349**
Estimated selling price range	$0.55 to 0.60/lb

Table 3.6 CRP Direct Processing Costs

Cost Component	Annual Cost ($)	Cost ($/lb)
Capital related @ 10%	350,000	0.0156
Non-labor operating and maintenance	300,000	0.0133
Labor (See Table 3.7)	804,960	0.0358
General overhead @ 125% of labor		0.0448
Solvent losses		0.0090
Catalyst screen replacement		0.0065
Other chemicals		0.0075
Packaging		0.0125
Total direct processing costs		**0.1450**

Table 3.7 CRP Labor Requirements and Costs

Number/Labor Category	Labor Rate ($/h)	Cost ($/Plant Operating Hour)
1/Material handler	10.00	10.00
2/Operators	8.50	17.00
2/Helpers	7.00	14.00
1/Lead operator/technician	15.00	15.00
1/Maintenance	18.00	18.00
1/Quality control	10.00	10.00
1/Packaging station operator	10.00	10.00
Subtotal direct labor		**99.00**
Fringes @ 30%		30.00
Total labor cost		**129.00**

3.5 Phase 2 Conclusions

The Neoprene/Dayco evaluations, and the successful reincorporation of regenerated prompt Neoprene compound waste at 5- and 10-phr levels, achieved properties equal to those of the 100% virgin polymer belt and hose compounds.

The economic analysis of the process projects an industry value for these recovered neoprene wastes at between \$0.55 and \$0.60/lb, with a 40% margin based on these price targets. These combined findings ensure a commercially viable future program for a full-scale 4,750-lb/h production facility, to be confirmed by the pilot-scale operation.

The processing trials and subsequent materials evaluation have confirmed that the solvents selected perform satisfactorily, can be reused continuously in the process with a 98.5% recovery and recycling level per pound of material recovered, and are within the acceptable U.S. Environmental Protection Agency and Occupational Safety and Health Administration requirements.

The stated objective of this industry research program was to determine whether industry should proceed with the pilot-scale operation of the CRP technology. On the basis of these findings, industry has elected to proceed with the pilot-scale operation of the process and to supply larger test quantities for user processing and customer evaluation/commercialization by the year 2000.

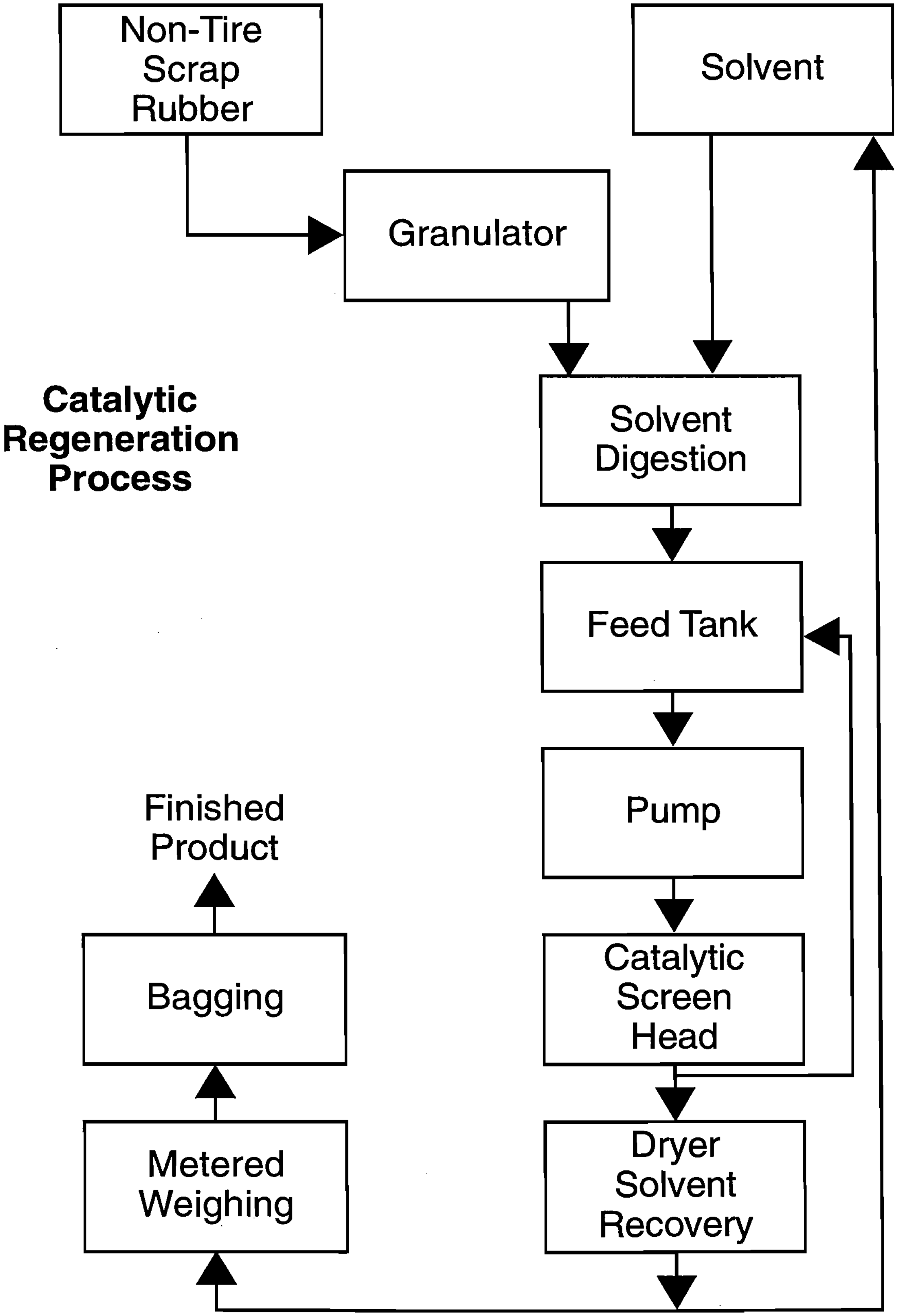

Figure 3.1 Basic Process Configuration: Catalytic Regeneration Process

Section 4
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Appendix A
Solvent Selection Research Report

"More Than Testing, We Care"

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Chemical Analysis & Particle Size Distribution of CRM Processed Materials

- PROJECT REPORT -

PN# 28211

By

Dr. Krishna C. Baranwal
Akron Rubber Development Laboratory, Inc.

December 1, 1997

cc: A. Goulart
L. Lima
F. Smith
P. Standley

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1. SUMMARY

Catalytically regenerated material (CRM) processing trials were run by Relastomer S/A in September and October of this year. Samples of CRM processed rubber, recovered solvents and slurry were collected.

In this project, we wanted to determine swelling efficiencies of recovered solvents, degree of devulcanization and any loss of rubber chemicals due to CRM processing. Also, we wanted to characterize resulting particles.

Analytical techniques used were GPC, HPLC, TLC, and FTIR for detection of polymers and rubber chemicals. Ro-Tap and LOM ultrasonic techniques were used for particle size characterization.

Swelling efficiencies of recovered solvents were equal to fresh solvents. Degree of devulcanization increased with CRM processing. For EPDM compound, maximum devulcanization after 5th pass was about 16% and for neoprene after 4th pass was about 43%. Residues obtained by drying filtered solvents from slurry showed no presence of polymers or curing agents. For neoprene, presence of antioxidant and antiozonant was observed. Particle sizes decreased with CRM processing. For EPDM, after 5th and final pass, most particles were in 4-12 micron range. For neoprene it was in 4-64 micron range. Undispersed particles showed heavy agglomeration whereas ultrasonic dispersion showed individual particles.

Recommendations are made for future work.

2. OBJECTIVES

Major objectives of this projects were: (a) to determine solvent swelling efficiencies of recovered solvents, (b) to determine degree of devulcanization as a function of processing, (c) to determine any loss of rubber chemicals in processing, and (d) to characterize particle size and particle size distributions of catalytically regenerated (CRM) processed dry materials.

3. BACKGROUND AND SAMPLES

Processing trials on EPDM and neoprene compound cryogenically ground materials were run by Prof. Lima in his pilot plant in Rio de Janeiro in September and October of this year. Paul Standley followed the trial on neoprene and Kris Baranwal followed the trial run on EPDM. See their trip reports [2,3] for details of processing trials. During these trials, samples were collected. Table 1 (a) gives details of EPDM-related samples. Similar samples were collected for neoprene compound and sample designations for this compound start with 6. For example:

6G40 means neoprene ground rubber-control
6GR1 means neoprene ground rubber through 1 pass, and
6GRF means neoprene ground rubber through final pass

Recovered solvents were obtained using reflux condensation method from slurry after each processing step. Filtered solvents were obtained by filtering slurry under vacuum using silica gel. For particle size characterization CRM powders were obtained after recovering solvent and drying the powder. Sheeted samples were used for density measurements and extractions.

4. CHEMICAL ANALYSIS

A. CROSSLINKING DENSITY; SWELLING METHOD

The objective here was to determine effects of CRM processing on crosslink density and, hence, devulcanization.

Three specimens from each sample were immersed in cyclohexane (EPDM) or in ethyl acetate (Neoprene) for 24 hours. The crosslinking density was calculated using the Flory-Rehner equation. Polymer-solvent interaction parameter was calculated using Bristow-Watson Equation. Data are listed in Table I and plotted in Figure 1.

$$\chi = \beta_1 + \frac{V_1 (\delta_1 - \delta_2)^2}{RT}$$

where:

χ = polymer-solvent interaction parameter
β_1 = lattice constant, usually 0.35±0.1
R = gas constant, 1.9858 cal/mole·K
δ_1, δ_2 = solubility parameter of polymer and solvent, respectively $(cal/cm^3)^{1/2}$
V_1 = molar volume of solvent, cm^3/mole
T = absolute temperature, K

TABLE I (a)

EPDM SAMPLES & THEIR DESIGNATIONS						
Pass No.	Date of Run	Slurry	Recovered Cyclohexane	Dry Powder	Sheet	Comments
0	--	--	Pure Cyclohexane (1 gallon)	ETA 2-G30 Powder	ETA 2-G30 Sheet	
I	9/30/97 thru 10/6/97	ETA 2-R1 Slurry	ETA 2-R1 Recovered Cyclohexane (1 liter)	ETA 2-R1 Powder	ETA 2-R1 Sheet	
II	10/6/97	ETA 2-R2 Slurry	ETA 2-R2 Recovered Cyclohexane (1 liter)	ETA 2-R2 Powder	ETA 2-R2 Sheet	
III	10/8/97	ETA 2-R3 Slurry	ETA 2-R3 Recovered Cyclohexane (1 liter)	ETA 2-R3 Powder	ETA 2-R3 Sheet	
IV	10/9/97	ETA 2-R4 Slurry	ETA 2-R4 Recovered Cyclohexane (1 liter)	ETA 2-R4 Powder	ETA 2-R4 Sheet	
V (Final)	10/9/97	ETA 2-RF Slurry	ETA 2-RF Recovered Cyclohexane (1 gallon)	ETA 2-RF Powder	ETA 2-RF Sheet	

TABLE I: CROSSLINK DENSITY DATA

POLYMER	SAMPLE	CROSSLINKING DENSITY, moles/cm^3
EPDM	Cured, unground EPDM	2.18x10^{-4}
	ETA-2G30	1.98x10^{-4}
	ETA-2R1	1.94x10^{-4}
	ETA-2R3	1.81x10^{-4}
	ETA-2RF	1.83x10^{-4}
NEOPRENE	Cured, unground Neoprene	5.52x10-4
	ETA-6G40	2.41x10-4
	ETA-6GR1	3.35x10-4
	ETA-6GR3	3.51x10-4
	ETA-6GRF	3.12x10-4

Crosslink density data for A (EPDM) and B (Neoprene) are plotted in Figures 1 and 2 respectively. In general, crosslink density decreased with CRM processing.

B. DEGREE OF DEVULCANIZATION

Degree of devulcanization was calculated from the data of crosslinking density of the unvulcanized samples and the vulcanized samples. The percentages of devulcanization were calculated using the following equation:

$$\%\ \text{Devulcanization} = \frac{\text{Crosslinking density of cured, unground sample (A)} \;-\; \text{Crosslinking density of devulcanized sample (B)}}{\text{Crosslinking density of cured, unground sample (A)}} \times 100$$

TABLE II. DEGREE OF DEVULCANIZATION

POLYMER	SAMPLE	% DEVULCANIZATION
EPDM	Cured, unground EPDM	0.00
	ETA-2G30	9.17
	ETA-2R1	11.01
	ETA-2R3	16.97
	ETA-2RF	16.06
NEOPRENE	Cured, unground Neoprene	0.00
	ETA-6G40	56.34
	ETA-6GR1	39.31
	ETA-6GR3	36.41
	ETA-6GRF	43.48

FIGURE 1

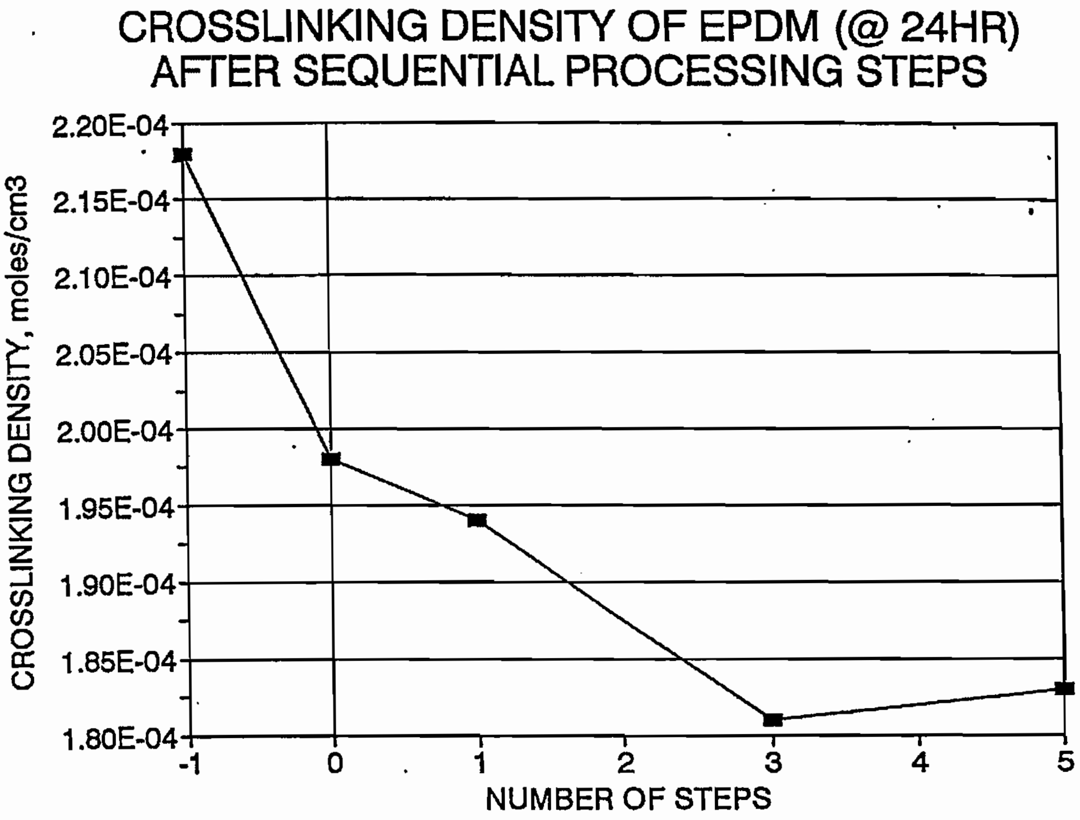
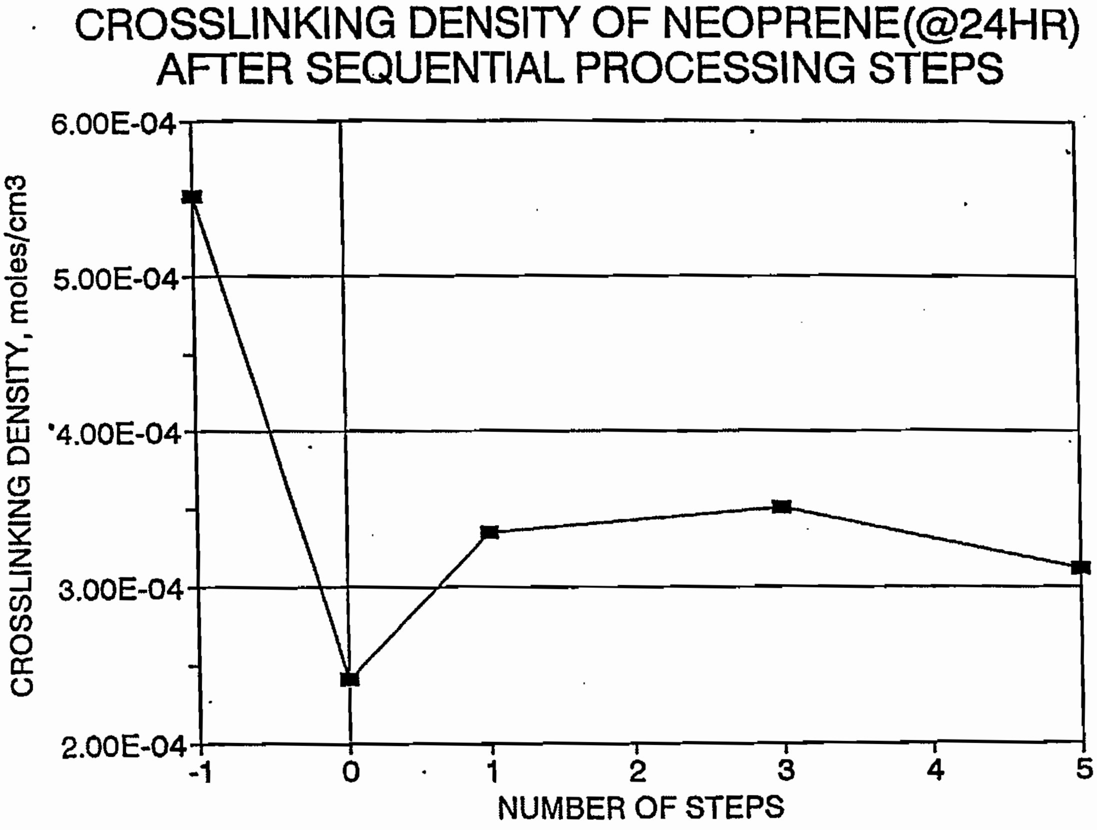

CROSSLINKING DENSITY OF EPDM (@ 24HR)
AFTER SEQUENTIAL PROCESSING STEPS
CROSSLINKING DENSITY, moles/cm3
2.20E-04
2.15E-04
2.10E-04
2.05E-04
2.00E-04
1.95E-04
1.90E-04
1.85E-04
1.80E-04
-1
0
1
2
3
4
5
NUMBER OF STEPS

FIGURE 2.


CROSSLINKING DENSITY OF NEOPRENE(@24HR)
AFTER SEQUENTIAL PROCESSING STEPS
CROSSLINKING DENSITY, moles/cm3
6.00E-04
5.00E-04
4.00E-04
3.00E-04
2.00E-04
-1
0
1
2
3
4
5
NUMBER OF STEPS

Data shown in Table II are plotted in Figures. 3 and 4. For EPDM, the degree of devulcanization increased with CRM processing. For neoprene, except for ETA-6G40, degree of devulcanization increased with processing. For EPDM, percent devulcanization after 5th and final pass was about 16% and for neoprene, after 4th pass, was 43%.

C. DENSITY; ASTM D 297-90

The density was measured per ASTM D 297-90 using sheet samples prepared by Prof. Lima by passing CRM powder obtained after solvent recovery through a 2-roll mill at room temperature. Pure ethanol was used instead of water because of wetting difficulties of water on the polymer surface. The specimens were immersed in ethanol for 24 hours before weighing in liquid (ethanol) to get rid of bubbles in the sheeted specimens.

Data are listed in Table III. For EPDM compounds, density remained the same for original as well as processed samples. For neoprene compound, except for the original sample (cured, unground) all have more or less same densities.

TABLE III. DENSITY OF CRM SHEET SAMPLES

POLYMER	SAMPLE	DENSITY, g/cm^3
EPDM	Cured, unground EPDM	1.2056
	ETA-2G30	1.2098
	ETA-2R1	1.2054
	ETA-2R3	1.2028
	ETA-2RF	1.2080
NEOPRENE	Cured, unground Neoprene	1.4095
	ETA-6G40	1.2788
	ETA-6GR1	1.3176
	ETA-6GR3	1.2804
	ETA-6GRF	1.3246

D. SWELLING EFFICIENCIES OF SOLVENTS

After each step of CRM processing, slurry was put in a laboratory dryer and solvent was recovered. Here, we wanted to determine the swelling efficiencies of fresh and recovered solvents.

Cured, unground specimens were swollen (EPDM compound in cyclohexane and neoprene in ethyl acetate) for 24 hours in fresh and recovered solvents (cyclohexane, ethyl acetate). Swelling efficiency was measured by determination of swelling ratio which was calculated using the following equation:

$$\text{Swelling ratio} = \frac{\text{Mass of swollen specimen}}{\text{Mass of cured, unground specimen}}$$

FIG. 3

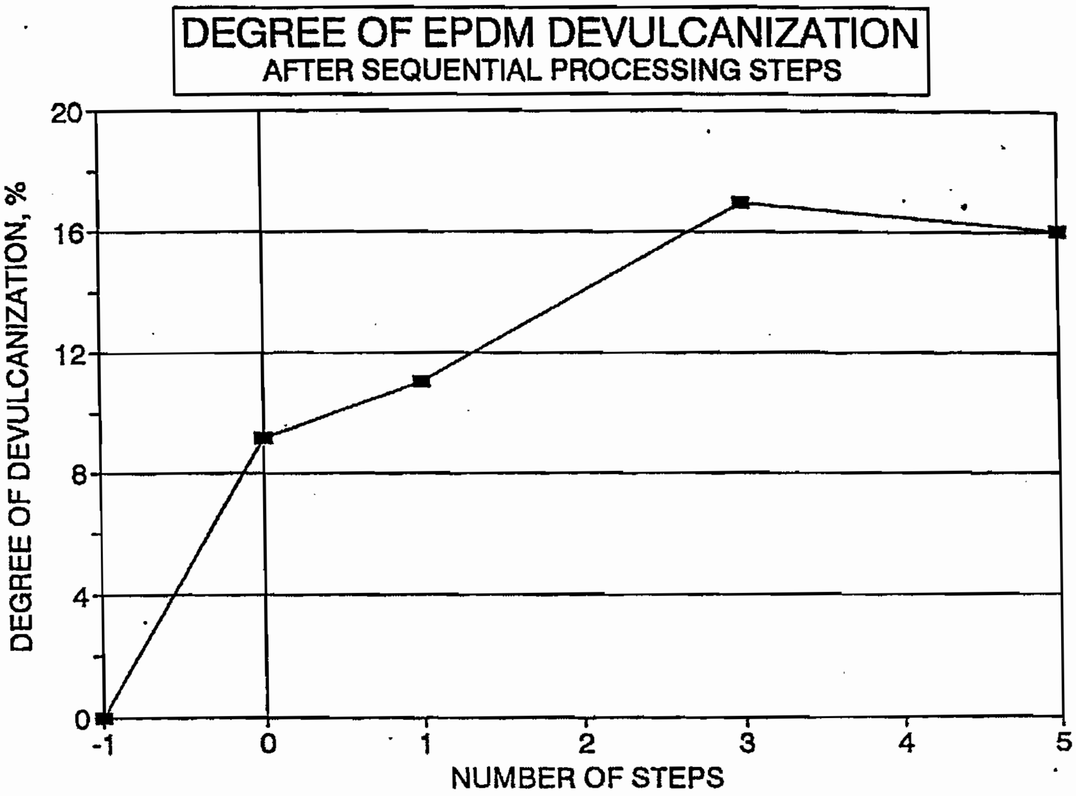
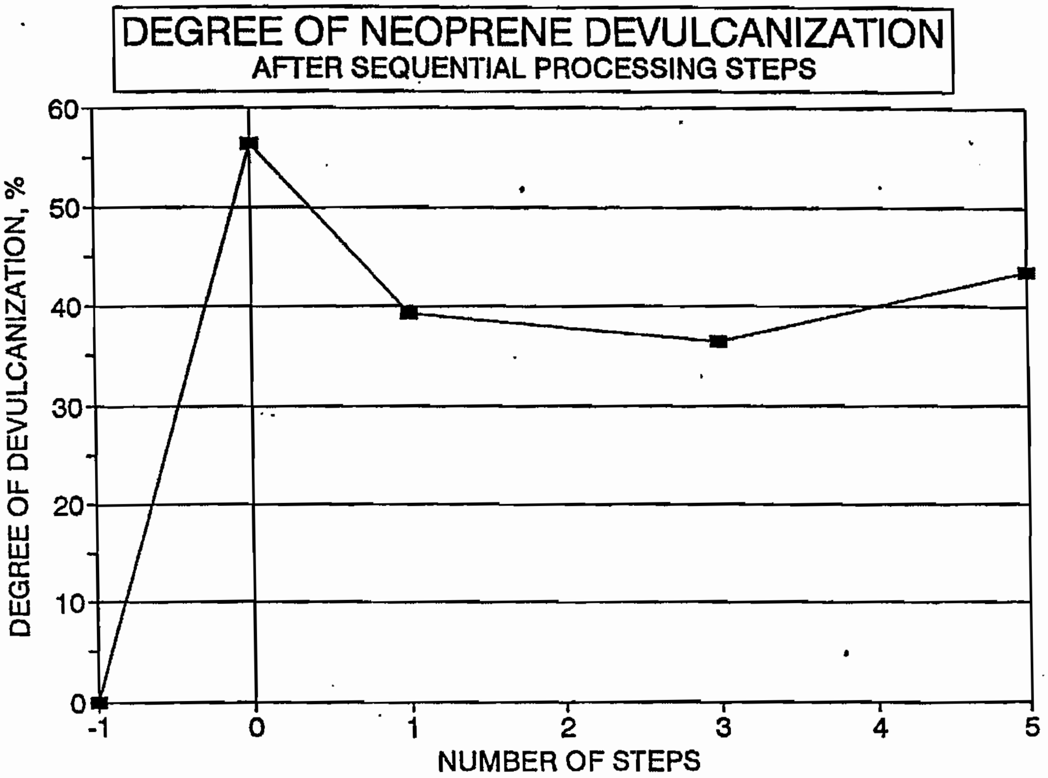

DEGREE OF EPDM DEVULCANIZATION
AFTER SEQUENTIAL PROCESSING STEPS
DEGREE OF DEVULCANIZATION, %
0
4
8
12
16
20
-1
0
1
2
3
4
5
NUMBER OF STEPS

FIG. 4


DEGREE OF NEOPRENE DEVULCANIZATION
AFTER SEQUENTIAL PROCESSING STEPS
DEGREE OF DEVULCANIZATION, %
0
10
20
30
40
50
60
-1
0
1
2
3
4
5
NUMBER OF STEPS

Data are listed in Tables IV and V.

TABLE IV. SWELLING EFFICIENCIES OF CYCLOHEXANE (EPDM)

Swelling Elapsed Time, Hours	Swelling Ratio of EPDM			
	Fresh Cyclohexane	Recovered Cyclohexane After		
		1-Pass	3-Pass	Final-Pass
0	1.0000	1.0000	1.0000	1.0000
1	1.4029	1.4079	1.3641	1.4046
2	1.5790	1.5794	1.5731	1.5835
4	1.6189	1.6214	1.6147	1.6207
6	1.5807	1.5856	1.5852	1.5813

TABLE V. SWELLING EFFICIENCIES OF ETHYL ACETATE (NEOPRENE)

Swelling Elapsed Time, Hours	Swelling Ratio of Neoprene			
	Fresh Ethyl Acetate	Recovered Ethyl Acetate After		
		1-Pass	3-Pass	Final-Pass
0	1.0000	1.0000	1.0000	1.0000
1	1.1712	1.1763	1.1758	1.1753
2	1.2594	1.2602	1.2575	1.2546
4	1.3692	1.3636	1.3571	1.3566
6	1.3993	1.3893	1.3820	1.3814

Swelling data for EPDM (ETA-R2) are plotted in Figure 5, and data for Neoprene (ETA-R6) are plotted in Figure 6. There is no difference in swelling efficiencies of fresh and recovered solvents either for cyclohexane or ethyl acetate.

E. RESIDUE CONTENTS IN FILTERED SOLVENTS FROM SLURRIES AND RECOVERED SOLVENTS AFTER FINAL PASS

Slurry, after each pass, was filtered using silica gel (Hi-Sil 233) under vacuum. Recovered cyclohexane and ethyl acetate, after final passes were used as received.

The specimen solvents (50 ml for each sample) were weighed and evaporated, followed by drying overnight in an oven at 70°C. Duplicate samples were run and average values are reported here. The percentage of the residue was calculated using the following equation:

$$\text{Percent Residue} = \frac{\text{Residual Mass}}{\text{Sample Mass}^{*}} \quad \text{x100}$$

Including solvent and residue

FIGURE 5

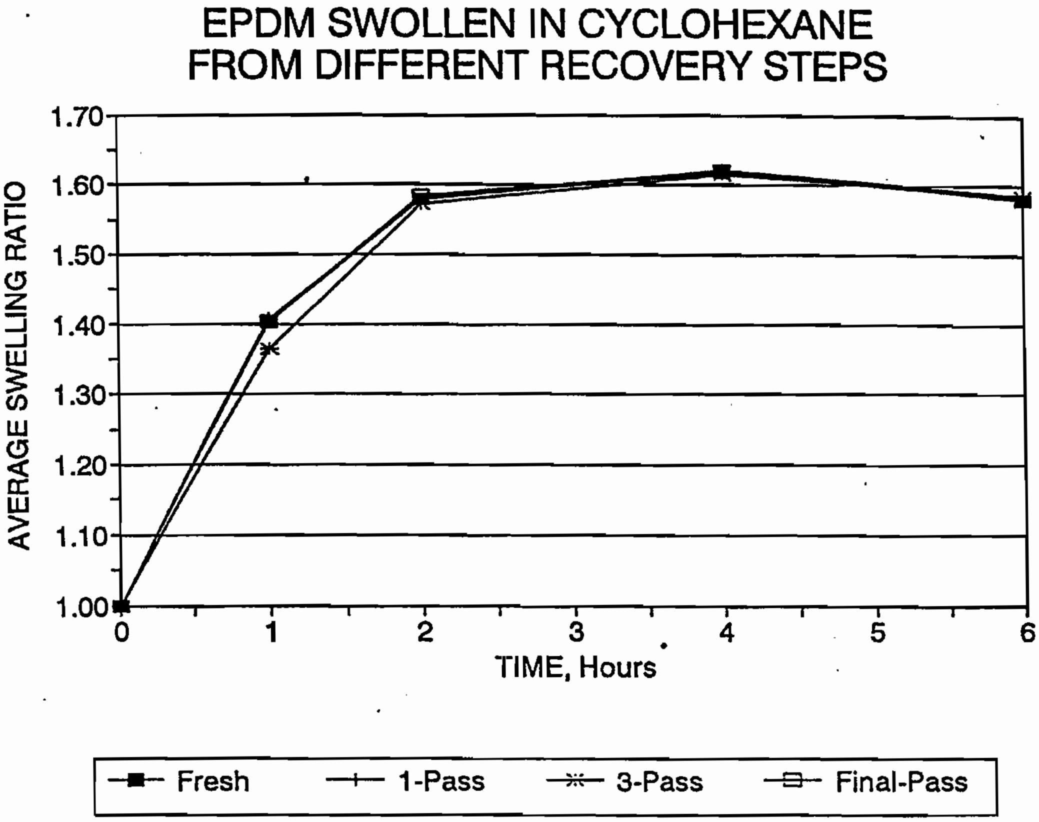
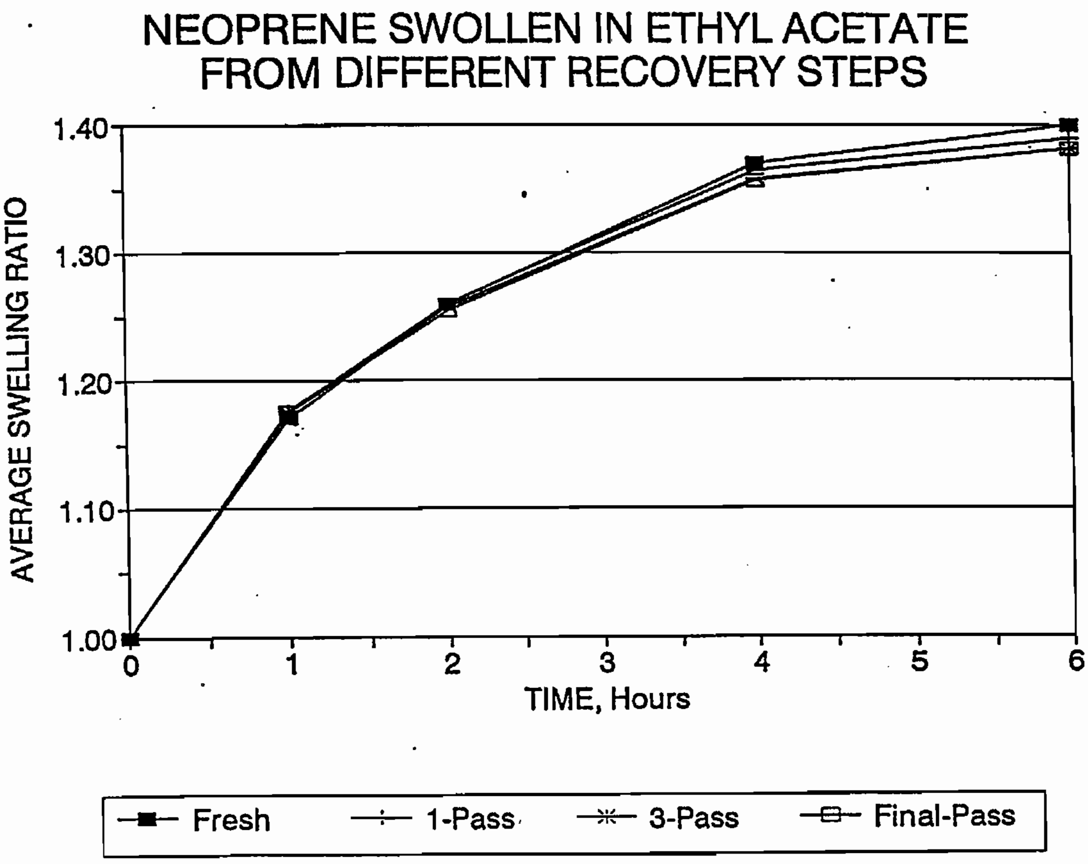

EPDM SWOLLEN IN CYCLOHEXANE
FROM DIFFERENT RECOVERY STEPS
AVERAGE SWELLING RATIO
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0
1
2
3
4
5
6
TIME, Hours
Fresh
1-Pass
3-Pass
Final-Pass

FIGURE 6


NEOPRENE SWOLLEN IN ETHYL ACETATE
FROM DIFFERENT RECOVERY STEPS
AVERAGE SWELLING RATIO
1.40
1.30
1.20
1.10
1.00
0
1
2
3
4
5
6
TIME, Hours
Fresh
1-Pass
3-Pass
Final-Pass

A. Cyclohexane

SAMPLE	RESIDUE, %
Fresh Cyclohexane	0.015
ETA-2R1 (from slurry)	7.222
ETA-2R3 (from slurry)	8.365
ETA-2RF (from slurry)	7.516
ETA-2RF (recovered after final pass)	0.014

B. Ethyl Acetate

SAMPLE	RESIDUE, %
Fresh Ethyl Acetate	0.021
ETA-6R2 (from slurry)	0.815
ETA-6R4 (from slurry)	0.735
ETA-6RF (recovered after final pass)	0.072

*Including solvent and residue.

As expected, fresh and recovered solvents have very little residues. EPDM compound slurry filtered solvents (after 1, 3 and final passes) contain about 7-8% residue. This may partly be done to the fact that EPDM has more oil and low oil fractions which might be filtered to give higher residues. Neoprene filtered solvents contain 0.7 - 0.8% residues.

These residues will be used to determine if some rubber chemicals and/or polymers are present.

F. MOLECULAR WEIGHT (MW) AND MOLECULAR WEIGHT DISTRIBUTIONS (MWD)

Residues from filtered solvents were run in GPC to determine MW and MWD of any polymeric materials present at 23°C in THF.

The top slurry in the sample can was filtered to remove any particulate materials followed by pipeting 50 ml of the filtrate using a pre-weighed flask. Another 50 ml of the filtrate was pipetted into a second flask for duplicate sampling. After drying almost to dryness on a hot plate, followed by further drying in an oven set at 70°C to a constant weight, the residue in a flask was reconstituted with tetrahydrofuran to a 25% W/V solution. Using a 250 ul syringe, the solution was withdrawn and injected into the HPLC through a 200 ul injector loop connected to a two-column Phenogel Linear Mixed Bed Column using the above conditions

GPC analysis results showed that there were no polymers in a detectable level in the solutions of the samples tested. See Table VI.

Also, no polymer was detected in residue in FTIR run.

TABLE VI. MW & MWD OF ANY POLYMERIC MATERIAL

POLYMER	SAMPLE	Mn; Mw; Mz; MWD
EPDM	ETA-2R0 ETA-2RF ETA-2R1 ETA-2R3	N/P N/P N/P N/P
NEOPRENE	ETA-6R0 ETA-6R2 ETA-6R4	N/P N/P N/P

NOTE: N/P denotes No Presence of Polymer

G. IDENTIFICATION OF CURATIVES & ANTIDEGRADANTS IN RESIDUES

HPLC analysis was carried out at 23°C using Perkin Elmer LC-235 Diode Array Detector @ 255 nm and 280 nm on the residues in the second flask. Chloroform was quantitatively added to the residues and it was analyzed by HPLC for chemicals identification and quantification using the conditions above.

HPLC analysis results showed that sulfur, TMTD, and MBTS (added in EPDM compound ETA-2G30) were not detected in the extracts of ETA-2R0, ETA-2R1, ETA-2R3, and ETA-2RF. See Table VII for data.

HPLC analysis of samples ETA-6R0, ETA-6R2, and ETA-6R4 showed that Octamine and Wingstay 100 (used in ETA-6R compound) are in samples ETA-6R2 and ETA-6R4 (see Table VII). These chemicals were not detected in sample ETA-6R0.

TABLE VII. CHEMICAL IDENTIFICATION BY HPLC

POLYMER	SAMPLE	SULFUR %	TMTD %	MBTS %	OCTAMINE %	WINGSTAY 100 %
EPDM	ETA-2R0* ETA-2R1 ETA-2R3 ETA-2RF	ND ND ND ND	ND ND ND ND	ND ND ND ND	— — — —	--- --- --- ---
NEOPRENE	ETA-6R0* ETA-6R2 ETA-6R4	--- --- ---	--- --- ---	--- --- ---	ND 0.57 0.62	ND 0.08 0.11

**Only Fresh Solvents* *ND denotes Not Detectable*

H. DETECTION OF ANTIDEGRADANTS BY THIN LAYER CHROMATOGRAPHY (TLC)

The residues were analyzed using TLC for antidegradants identification on EPDM and neoprene sets of samples. TLC plate was developed in a 90/10 heptane/ethyl acetate.

TLC analysis showed that only Octamine and Wingstay 100 were detected in the Neoprene samples. These results confirmed those obtained in the HPLC analysis.

I. QUANTIFICATION OF CURE SYSTEMS BY TLC

Thin Layer Chromatography was used to analyze qualitatively the accelerator fragments in the remaining residues in the flasks by converting them to chloride salt fragments with acid solution and spotting them on a TLC plate for development in the TLC tank. This method would detect the methyl and ethyl fragments, etc. in the residues (For example, methyl fragments from TMTD in the residues of sample ETA-2RF, ETA-2R1, and ETA-2R3 would be detected, if they were present). Also, ETU would be detected it is present in the residues of Samples ETA-6R2 and ETA-6R4

TABLE VIII. DETECTION OF METHYL FRAGMENTS

POLYMER	SAMPLE	METHYL FRAGMENT	ETU
EPDM	ETA-2R0	ND	N/A
	ETA-2R1	ND	N/A
	ETA-2R3	ND	N/A
	ETA-2RF	ND	N/A
NEOPRENE	ETA-6R0	N/A	ND
	ETA-6R2	N/A	ND
	ETA-6R4	N/A	ND

N/A denotes Not Applicable *ND denotes Not Detectable*

5. PARTICLE SIZE CHARACTERIZATION

A. RO-TAP PARTICLE SIZE DETERMINATION; ASTM D 5644-96

The specified sample size of 100 grams was not available for testing. The ratio of 100 parts of sample per 15 parts of talcum powder was maintained, however.

The particulate rubber and talcum powder were placed in a 500 ml jar and shaken for one minute until blended.

The mixed sample was poured onto the top of a stack of sieves, each of which contained two rubber balls. The sieve stack was placed on the shaker and activated. After 20 minutes had elapsed, the sieves were removed from the shaker, and the contents of each weighed. The percent on each sieve was calculated, based on the original sample weight. Data are shown in Table IX.

TABLE IX. PARTICLE SIZE DISTRIBUTION; ASTM D 5644-96*

SAMPLE	SIEVE NUMBER												
	20	30	40	50	60	100	120	140	200	230	325	400	Pan
EPDM 2G30 Retained, %	0.0	0.1	8.2		35.3	24.7	5.9						25.8
2R1 Retained, %		0.0	7.1			69.1				18.0	2.8	3.2	0.0
2R3 Retained, %		0.1	0.7			66.3				27.4	3.5	2.0	0.0
2RF Retained, %			trace	1.8		39.4				42.7	10.7	5.4	0.0
NEOPRENE 6G40 Retained, %		0.0	1.2		8.2	17.2	11.7	13.0					48.8
6R1 Retained, %		0.0	0.2		9.3	15.1			22.8		31.6		20.9
6R3 Retained, %			0.0	2.2		23.2			15.8		31.9	7.9	19.1
6RF Retained, %				0.0	1.2	14.1				32.7	25.6	10.7	15.7

*The required 100 gram sample was not available for testing. The talc was added proportionally based on the sample weight.

Bar graphs are shown in Figures 7-10 for EPDM powders and in Figures 11-14 for neoprene powders. For both systems, finer particles are obtained with increase in number of processing steps.

B. LIGHT OPTICAL MICROSCOPE (LOM) AND ULTRASONIC TECHNIQUE

SAMPLE PREPARATION

The samples of EPDM ground rubber were ultrasonically dispersed in acetone, then diluted with mineral oil, and then further dispersed in an ultrasonic bath. Four drops of this diluted oil solution were then placed on a clean glass microscope slide with a cover slip placed over the top. The samples of neoprene ground rubber were ultrasonically dispersed in acetone, diluted with acetone, and then further dispersed in an ultrasonic bath. Four drops of this were placed on a clean glass microscope slide, and the solvent allowed to evaporate.

ANALYSIS

The samples were then analyzed with transmitted light at 60X and 100X (for the fine particles) magnification using an Olympus Zoom Stereomicroscope model SZ 60 interfaced with a Sony CCD high resolution color video camera. The micrograph of the dispersed particles was then

FIGURE 7

ETA ENVIRONMENTAL P/N 28211 SAMPLE 2G30 ROTAP PARTICLE SIZE DISTRIBUTION

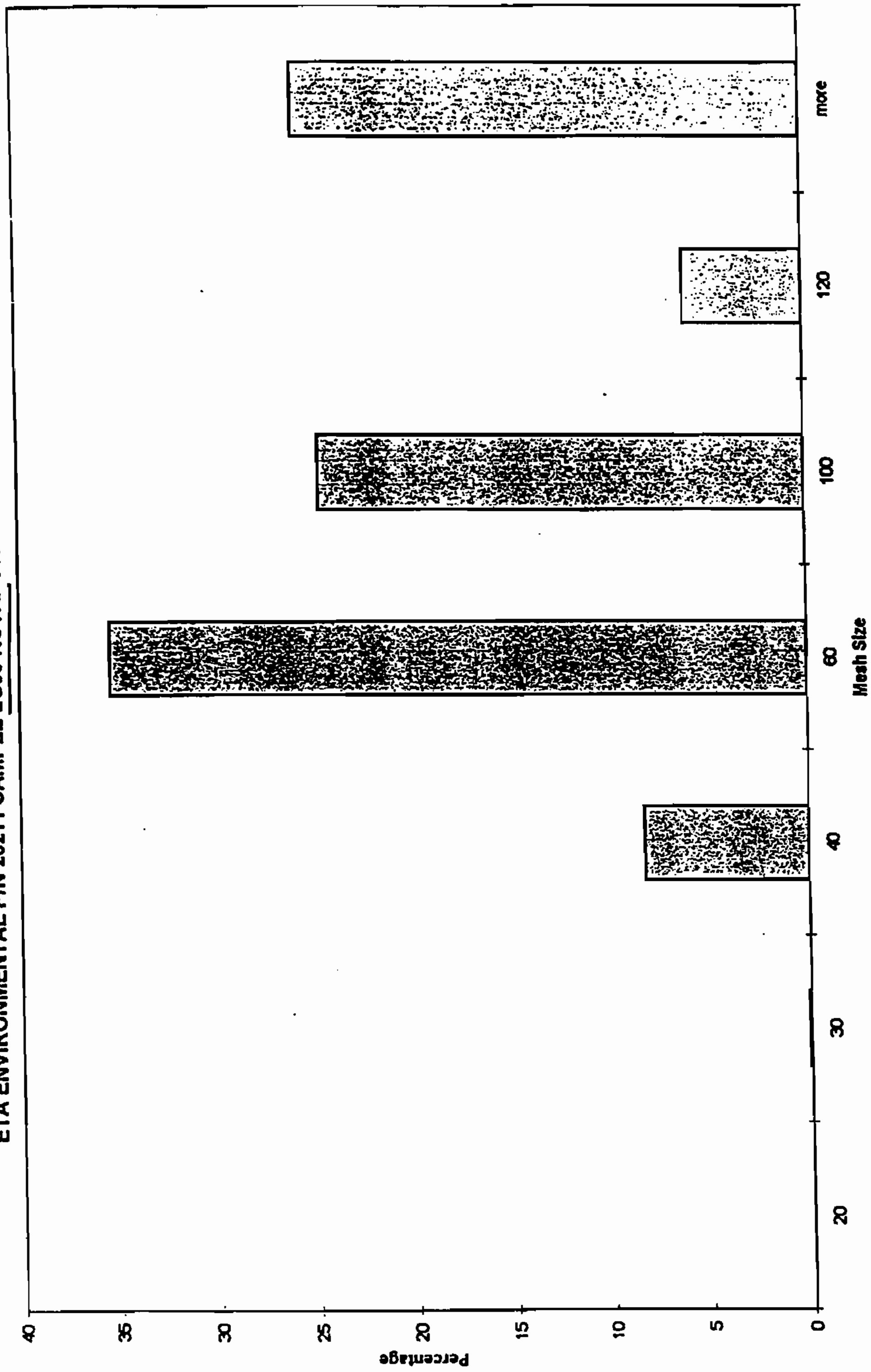


FIGURE 8

ETA ENVIRONMENTAL P/N 28211 SAMPLE 2R1 ROTAP PARTICLE SIZE DISTRIBUTION

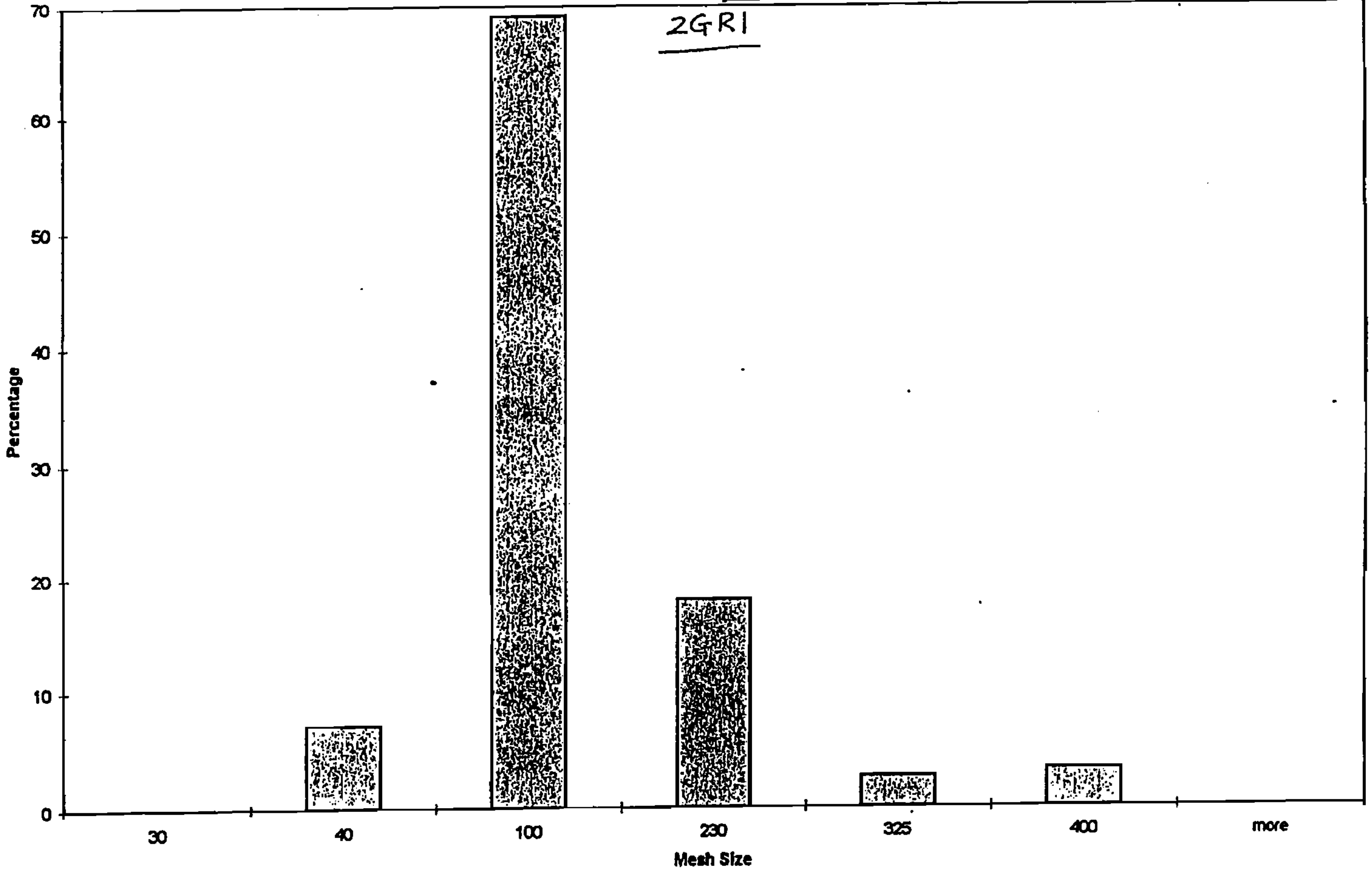

2GR1

FIGURE 9

ETA ENVIRONMENTAL P/N 28211 SAMPLE 2R3 ROTAP PARTICLE SIZE DISTRIBUTION

2GR3

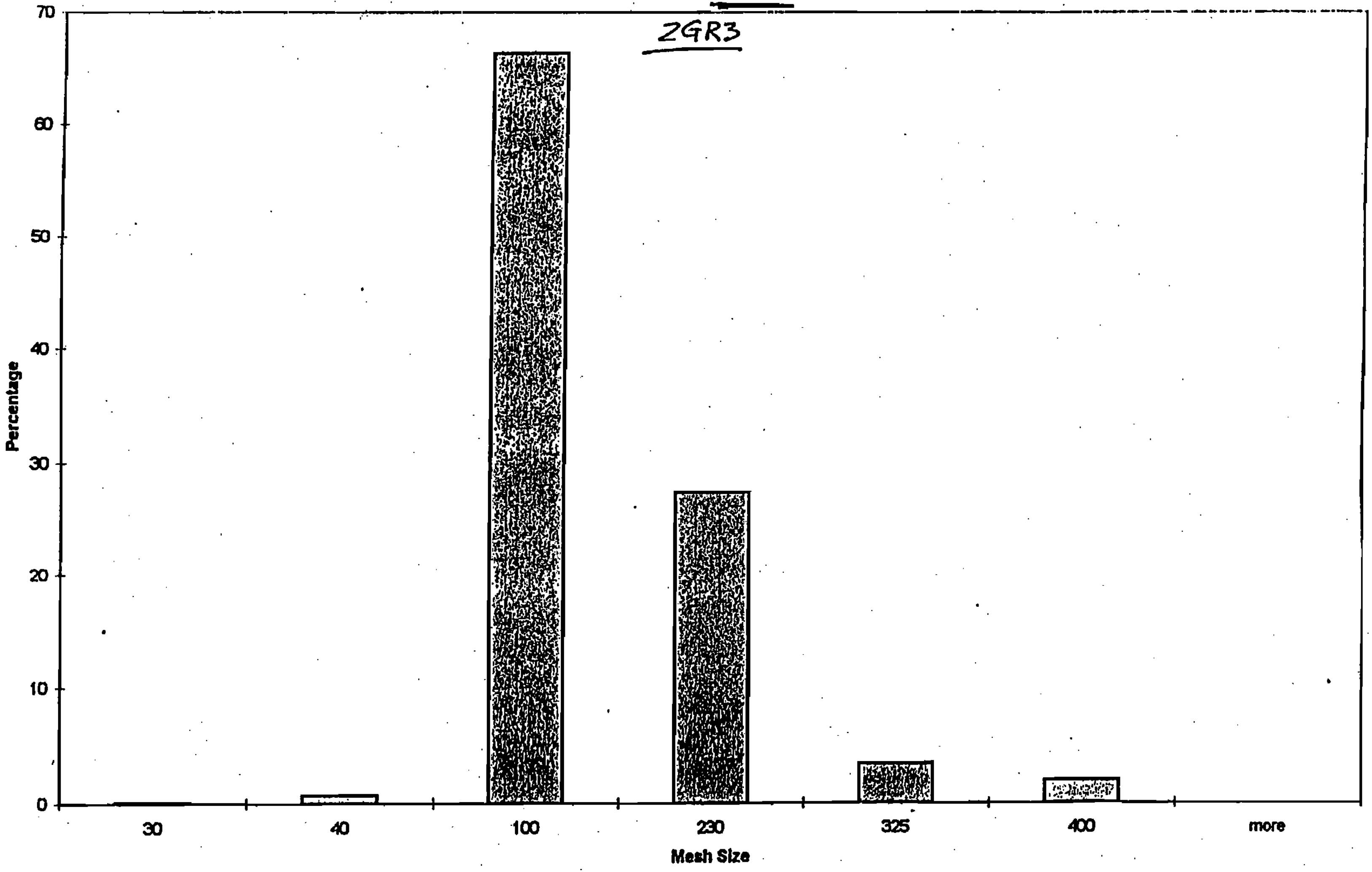


FIGURE 10

ETA ENVIRONMENTAL P/N 28211 SAMPLE 2RF ROTAP PARTICLE SIZE DISTRIBUTION

2GRF

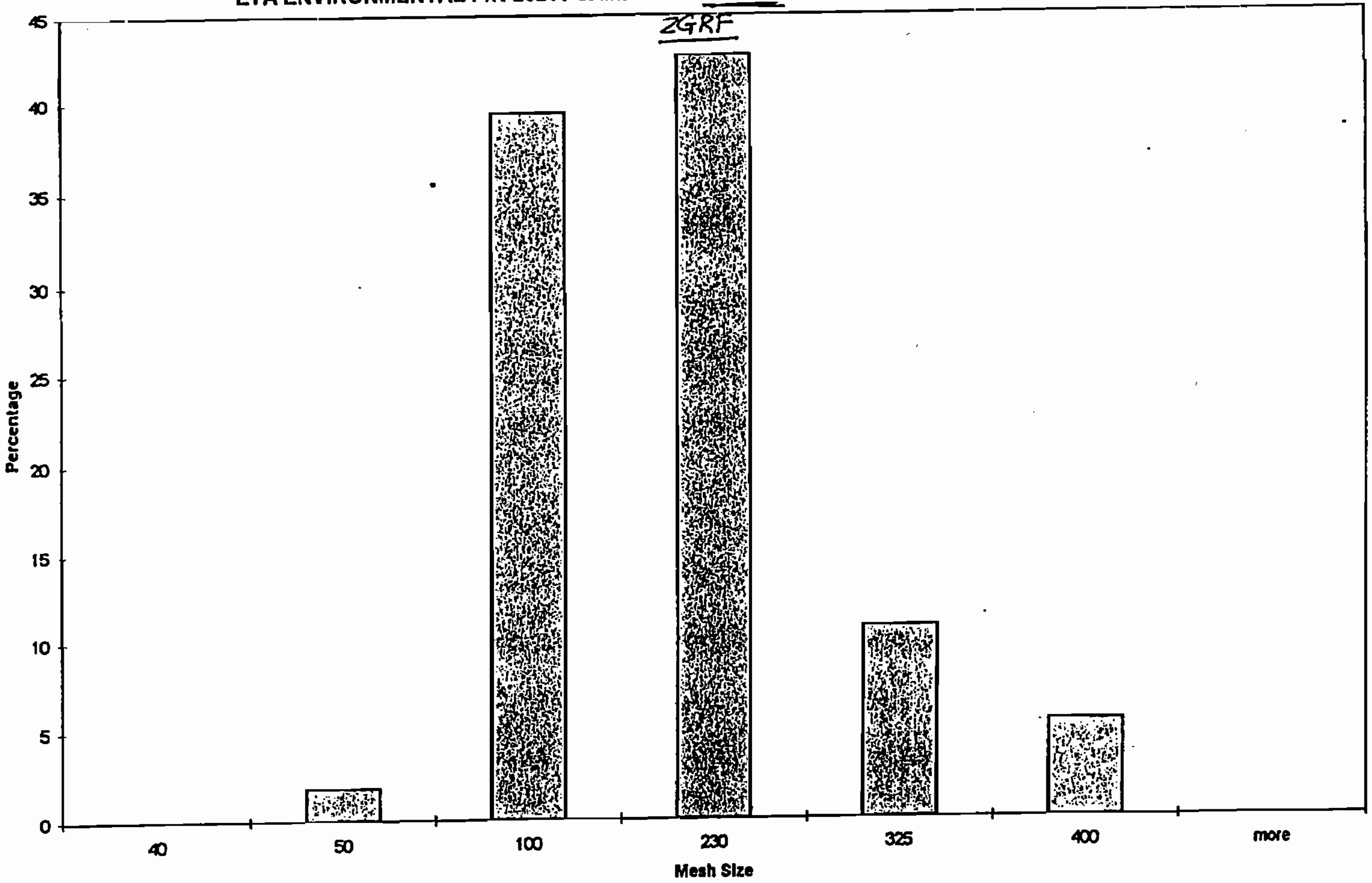


FIGURE 11

ETA ENVIRONMENTAL P/N 28211 SAMPLE 6G40 ROTAP PARTICLE SIZE DISTRIBUTION

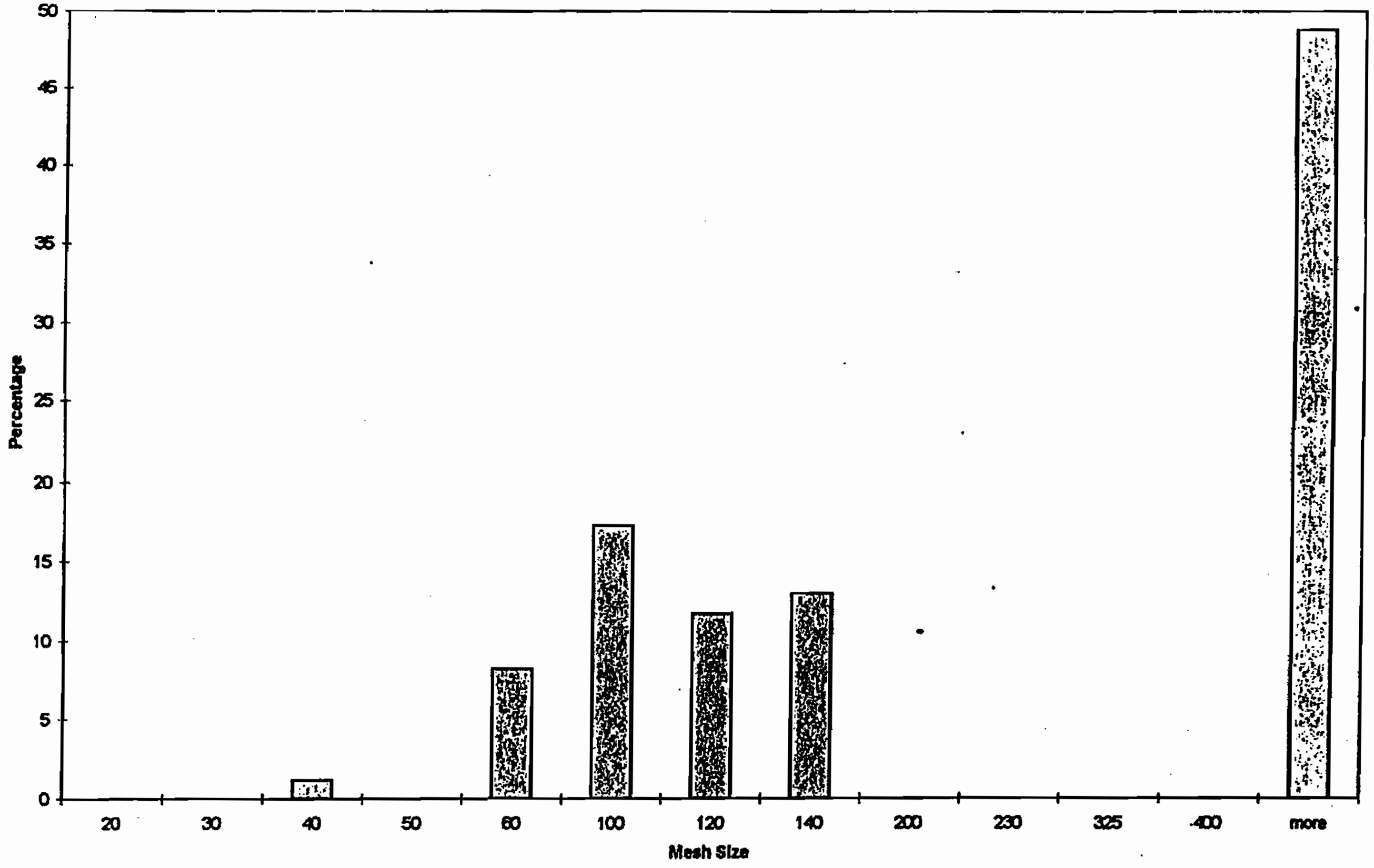


FIGURE 12

ETA ENVIRONMENTAL P/N 28211 SAMPLE GR1 ROTAP PARTICLE SIZE DISTRIBUTION

6GR1

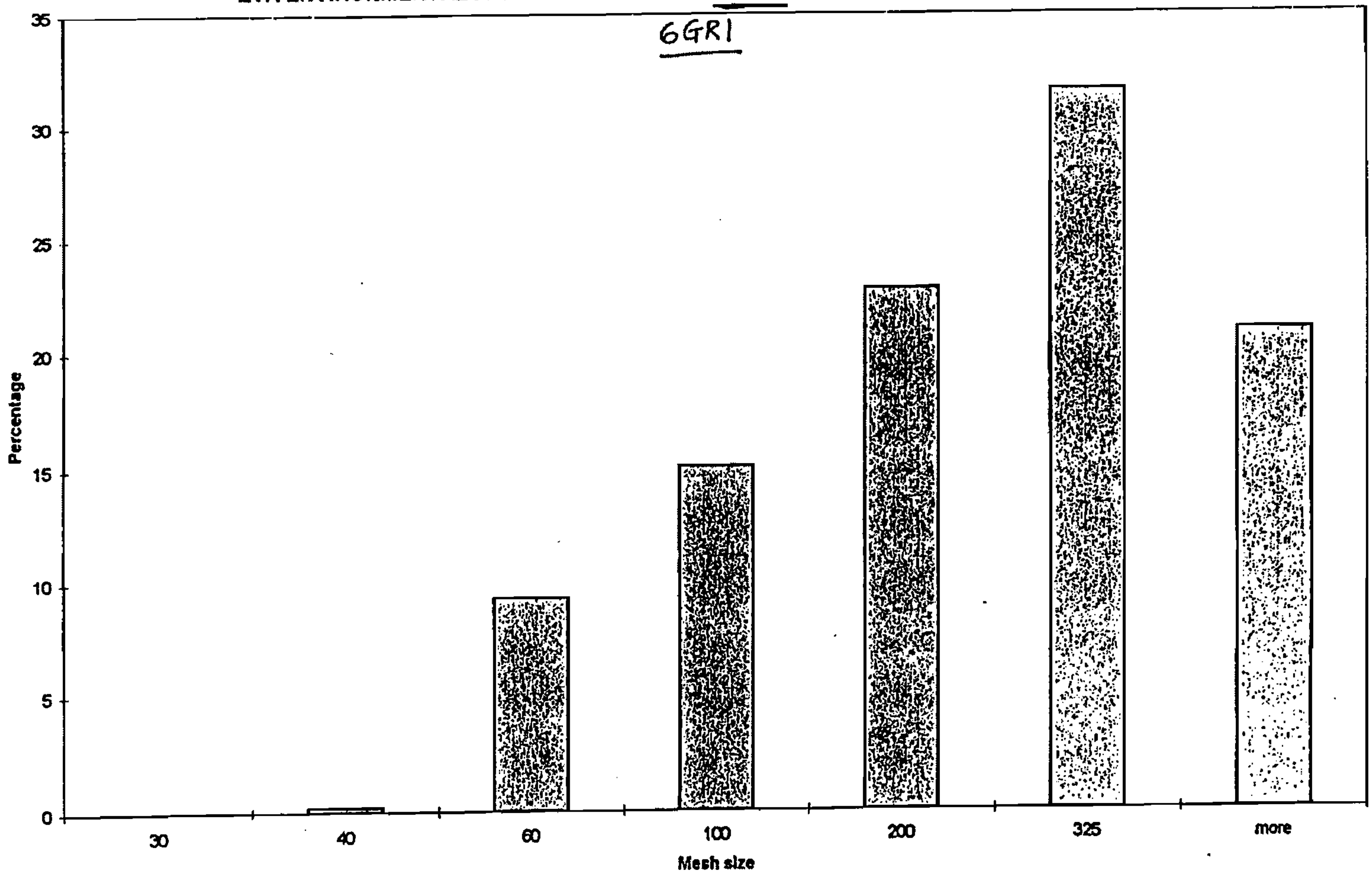


FIGURE 13

ETA ENVIRONMENTAL P/N 28211 SAMPLE 6R3 ROTAP PARTICLE SIZE DISTRIBUTION

6GR3

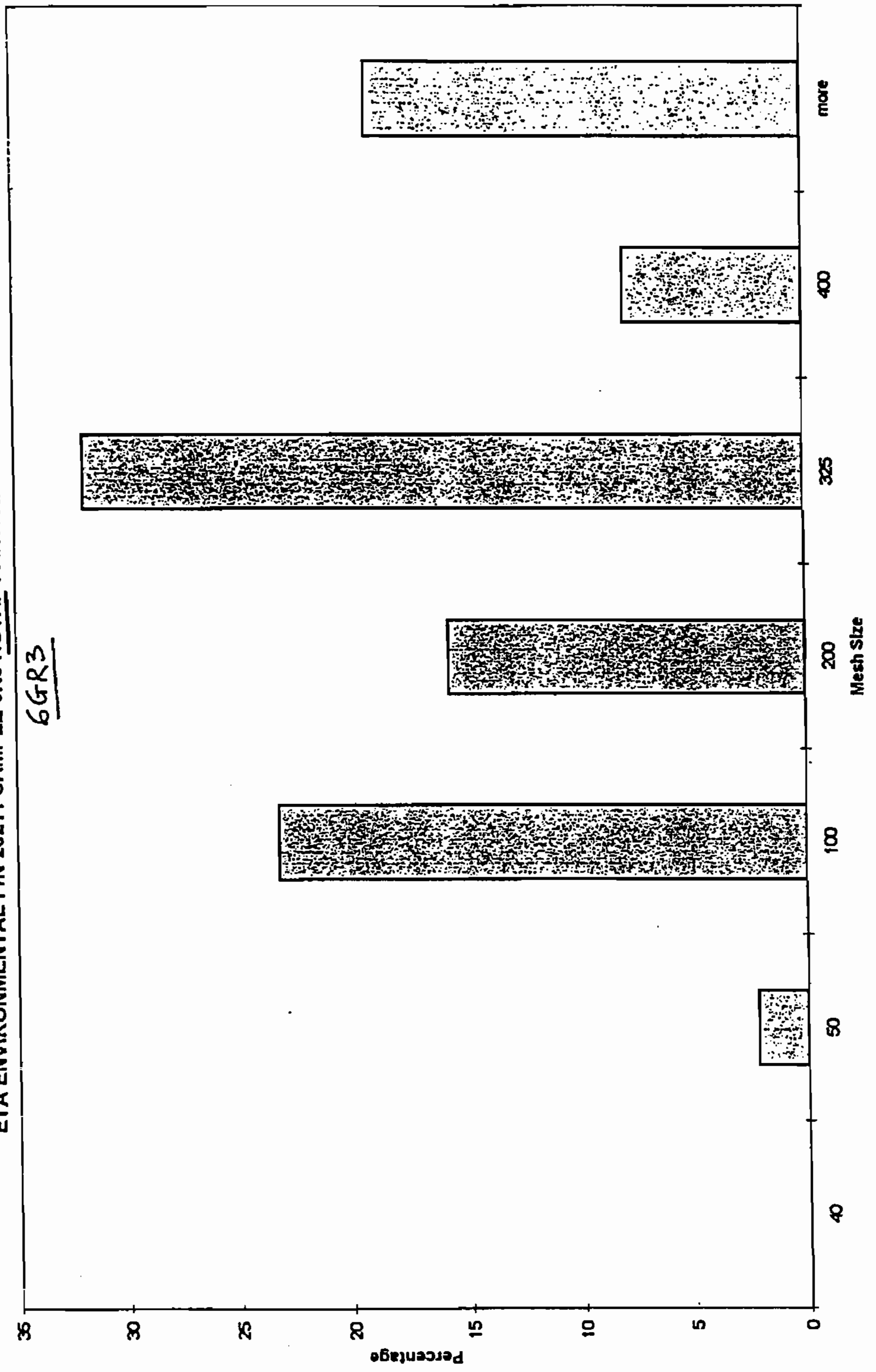
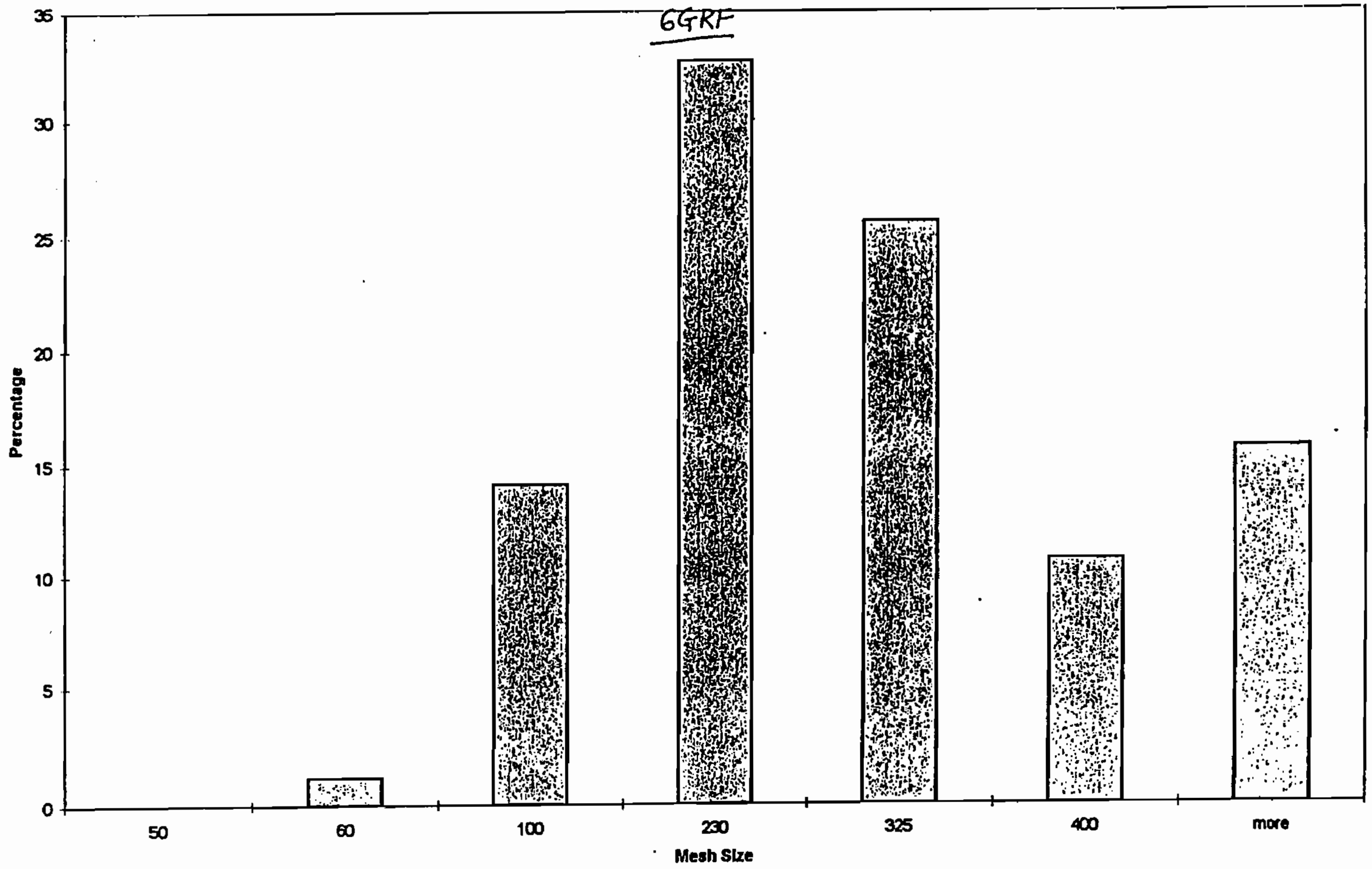


FIGURE 14

ETA ENVIRONMENTAL P/N 28211 SAMPLE 6RF ROTAP PARTICLE SIZE DISTRIBUTION

6GRF



saved using Mediacapture© imaging software and the diameters of the non-spherical particles were determined using Scion Corporation Image (version beta 1a) software on an IBM computer. The non-spherical particles were mathematically converted to spheres and then the diameter of these spheres was calculated . The diameter data was then transferred to an EXCEL spreadsheet and analyzed to generate particle size distribution and histogram information.

TABLE X. LOM-ULTRASONIC PARTICLE SIZE DATA

Sample	Average Particle Size, µm	Standard Deviation	n (number of particles counted)	Maximum Particle Size, µm	Minimum Particle Size, µm	Range
EPDM						
ETA-2G30	43.37	67.41	200	752.77	6.92	745.84
ETA-2R1	59.69	72.62	200	515.50	6.92	508.57
ETA-2R3	49.85	69.08	200	426.21	6.95	419.26
ETA-2RF	24.20	34.64	200	239.62	3.99	235.63
NEOPRENE	51.56	36.63	200	230.49	6.95	223.55
ETA-6G40						
ETA-6GR1	47.83	36.62	200	182.91	6.95	175.96
ETA-6GR3	49.23	38.51	200	277.94	6.92	271.01
ETA-6GRF	32.26	42.01	200	275.76	3.99	275.76

Particle size distribution histograms for EPDM samples are shown in Figures 15-19. From these histograms it is clear that with CRM processing, particle size decreases. For the final pass, most particles are between 2-12 microns (Figure 19). In fact large tail seen in Figure 18 (R3 processing step) disappeared in the final, 5th, pass (Figure 19).

Figures 20-23 are histograms for neoprene compounds. Again, with processing, particle sizes decreased. Finest screen used for neoprene was 80-mesh whereas for EPDM was 250-mesh. Most particle sizes are in the 4-64 micron range.

C. PHOTOMICROGRAPHS BY LIGHT OPTICAL MICROSCOPE (LOM): (DISPERSED AND "AS-RECEIVED" SAMPLES)

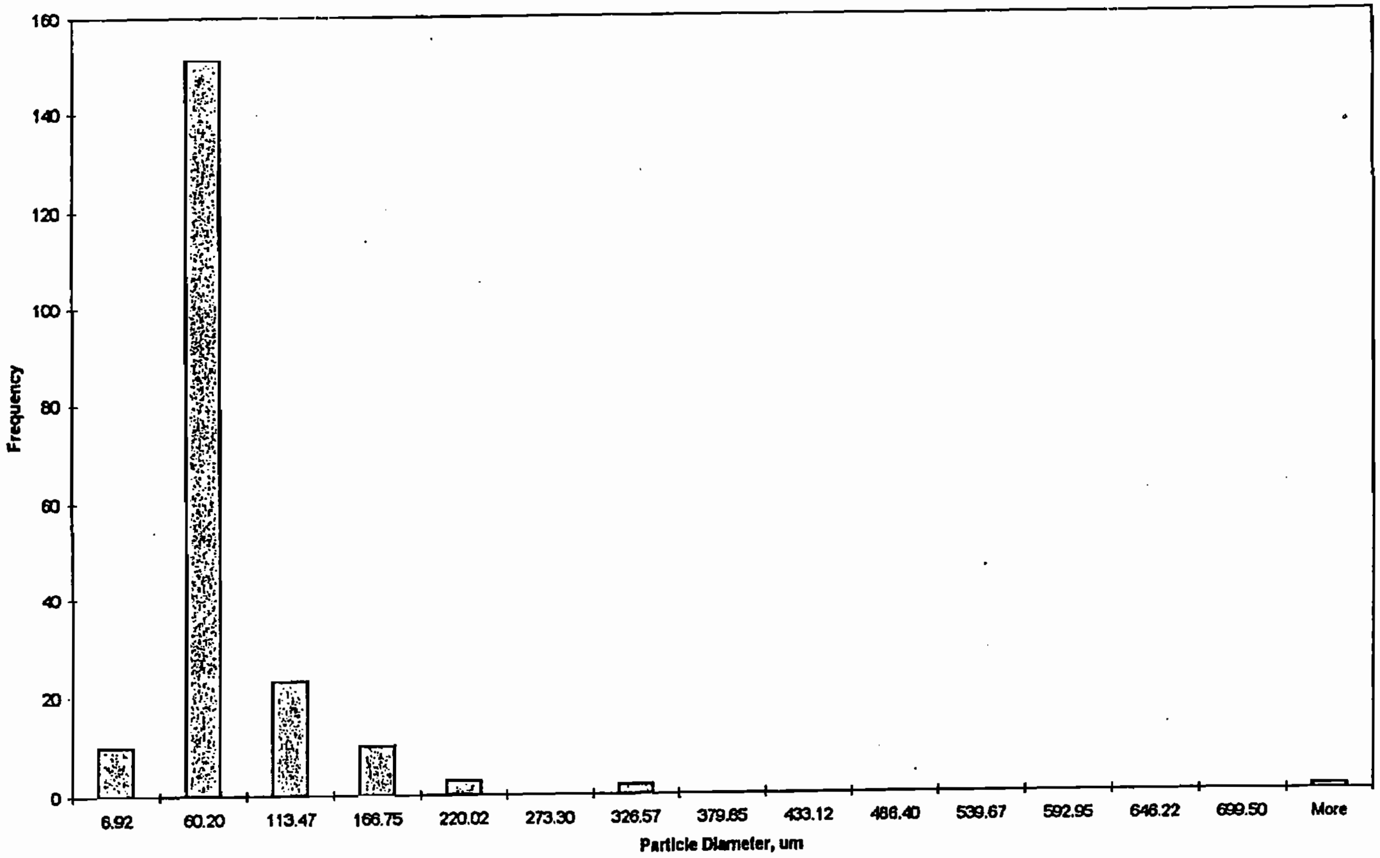
Photomicrographs were taken of the samples with an Olympus Zoom stereo microscope model SZ 60, interfaced with a Sony CCD IRIS high resolution video camera and a Sony color video printer at 20X magnification using both transmitted light and reflected light.

The transmitted light photomicrographs are of the ultrasonically dispersed samples and the reflected light photomicrographs are of the "as-received" ground rubber cast on a glass microscope slide. The neoprene samples were observed to contain fibers which were generally absent from the EPDM samples. Enclosed are the photomicrographs of the samples.

ETA ENVIRONMENTAL P/N 28211 SAMPLE 2G30 EPDM GROUND RUBBER PARTICLE SIZE DISTRIBUTION

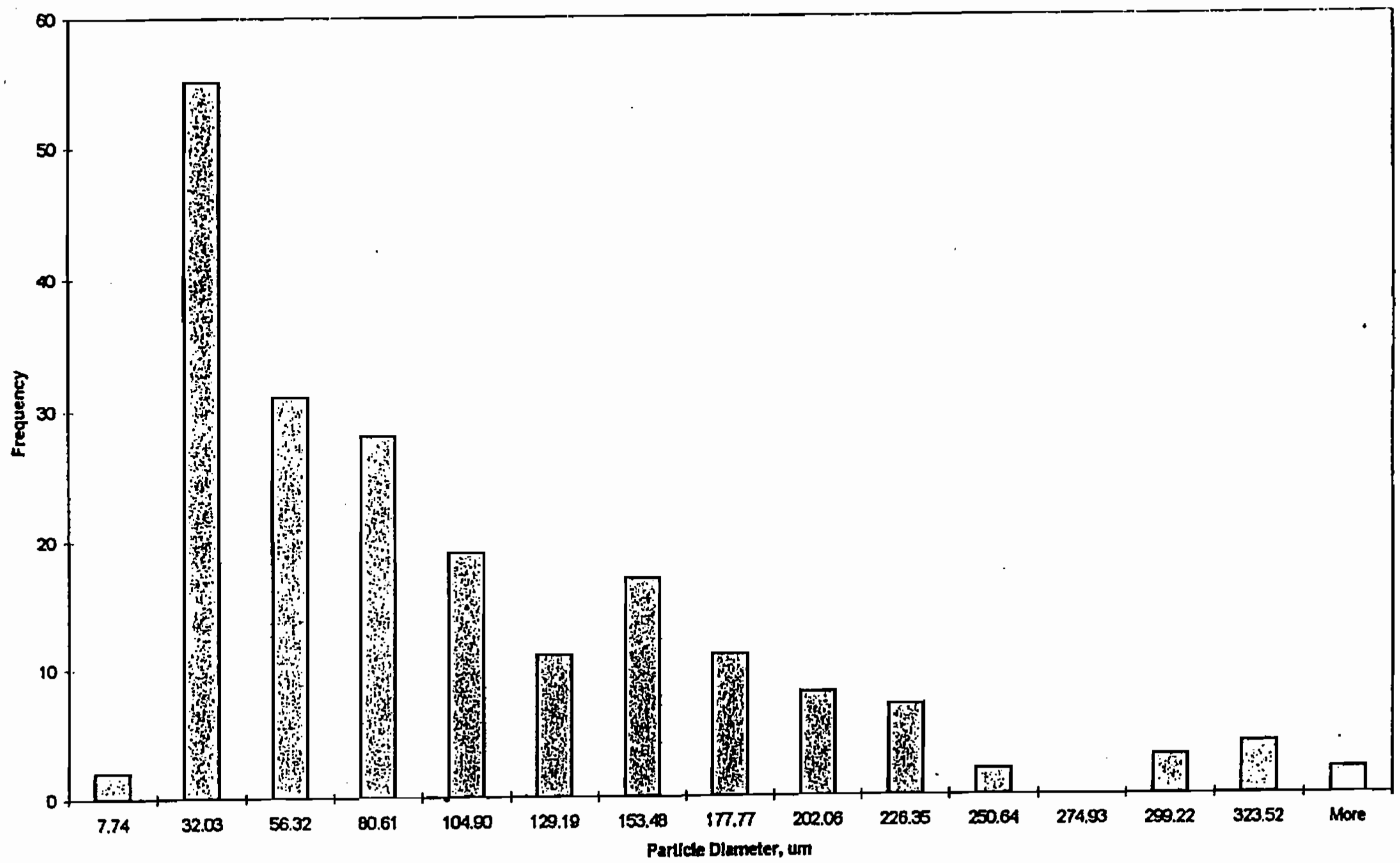
Ground rubber — control

Figure 15 Histogram



ETA ENVIRONMENTAL P/N 28211 SAMPLE 2G30R1 EPDM GROUND RUBBER PARTICLE SIZE DISTRIBUTION

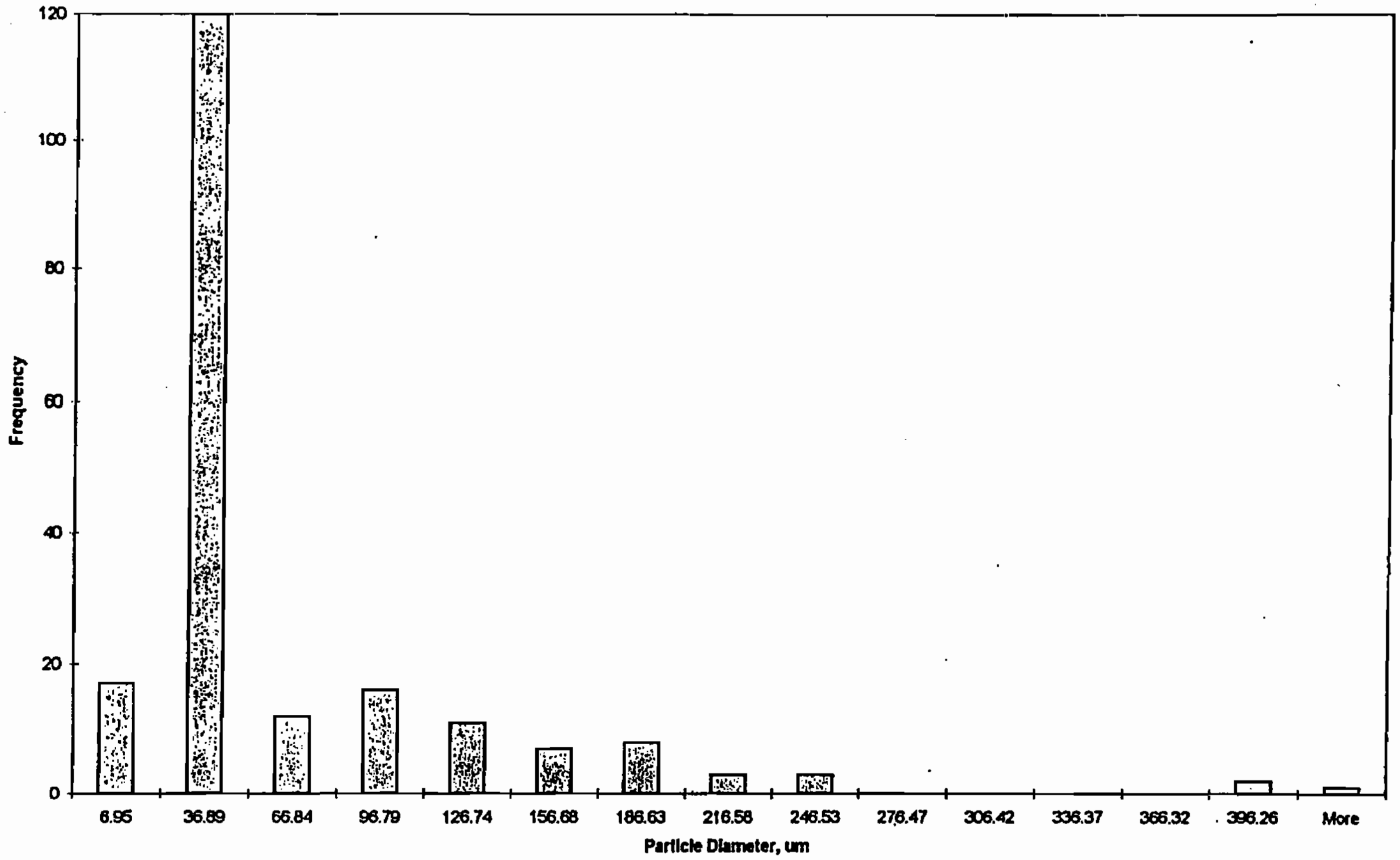
Figure 16 **Histogram**



ETA ENVIRONMENTAL P/N 28211 SAMPLE 2R3 GROUND RUBBER PARTICLE SIZE DIAMETER

EPDM

FIGURE 17 **Histogram**

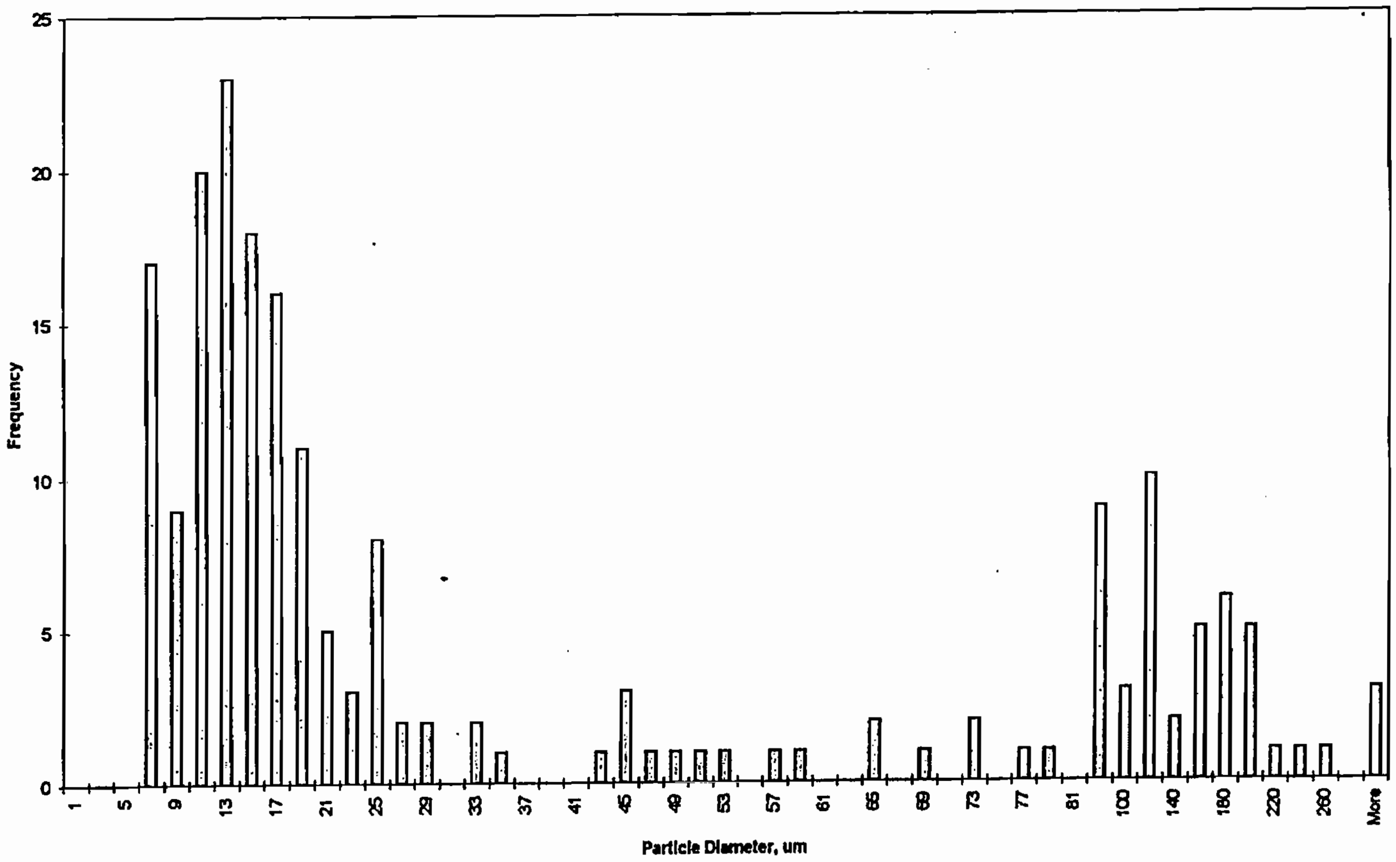


ETA ENVIRONMENTAL P/N 28211 SAMPLE 2R3 EPDM GROUND RUBBER PARTICLE SIZE DISTRIBUTION

FIGURE 18

Histogram

(EXPANDED VERSION OF FIGURE 17)

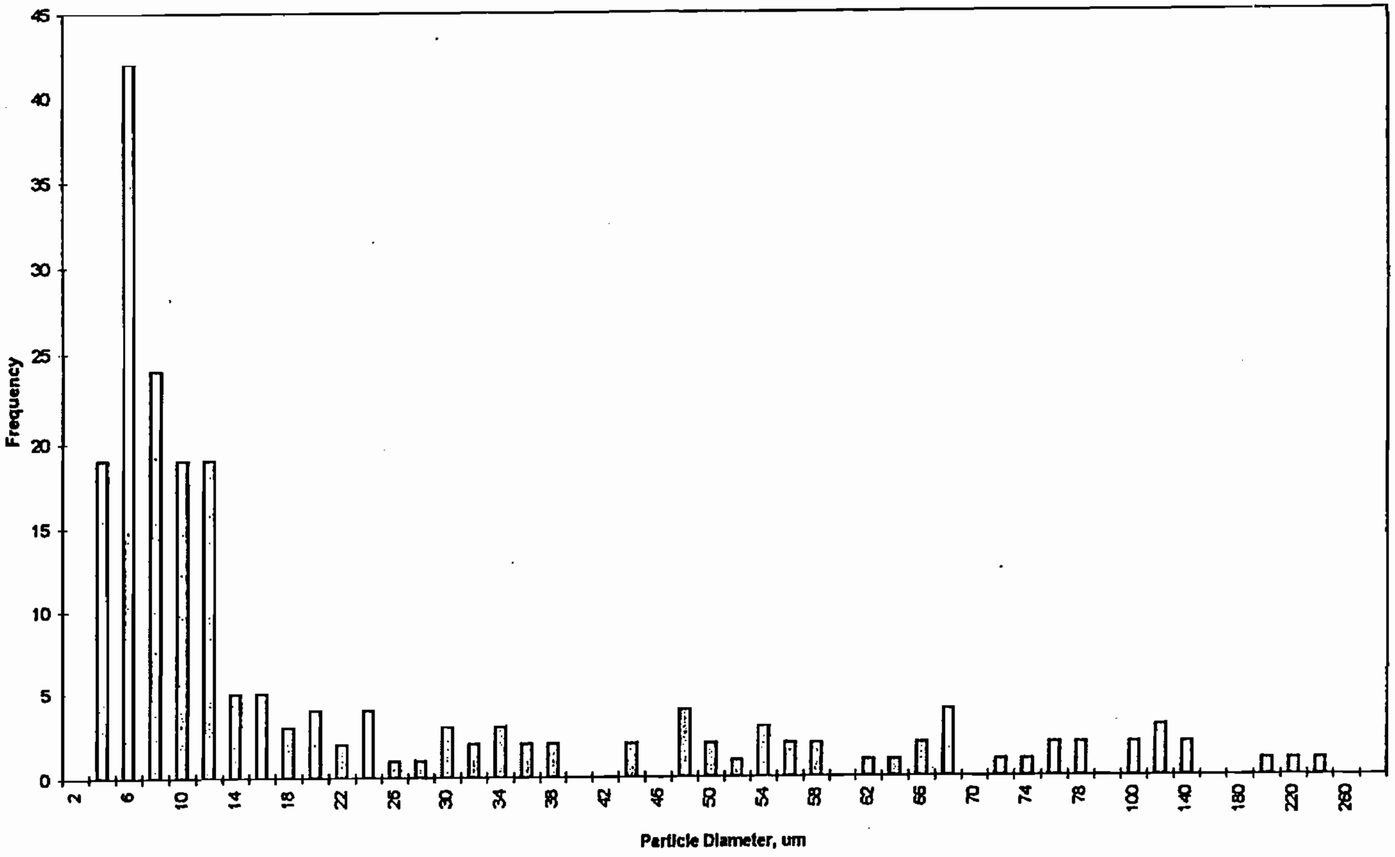


ETA ENVIRONMENTAL P/N 28211 SAMPLE 2RF EPDM GROUND RUBBER PARTICLE SIZE DISTRIBUTION

Final Pass

FIGURE 19

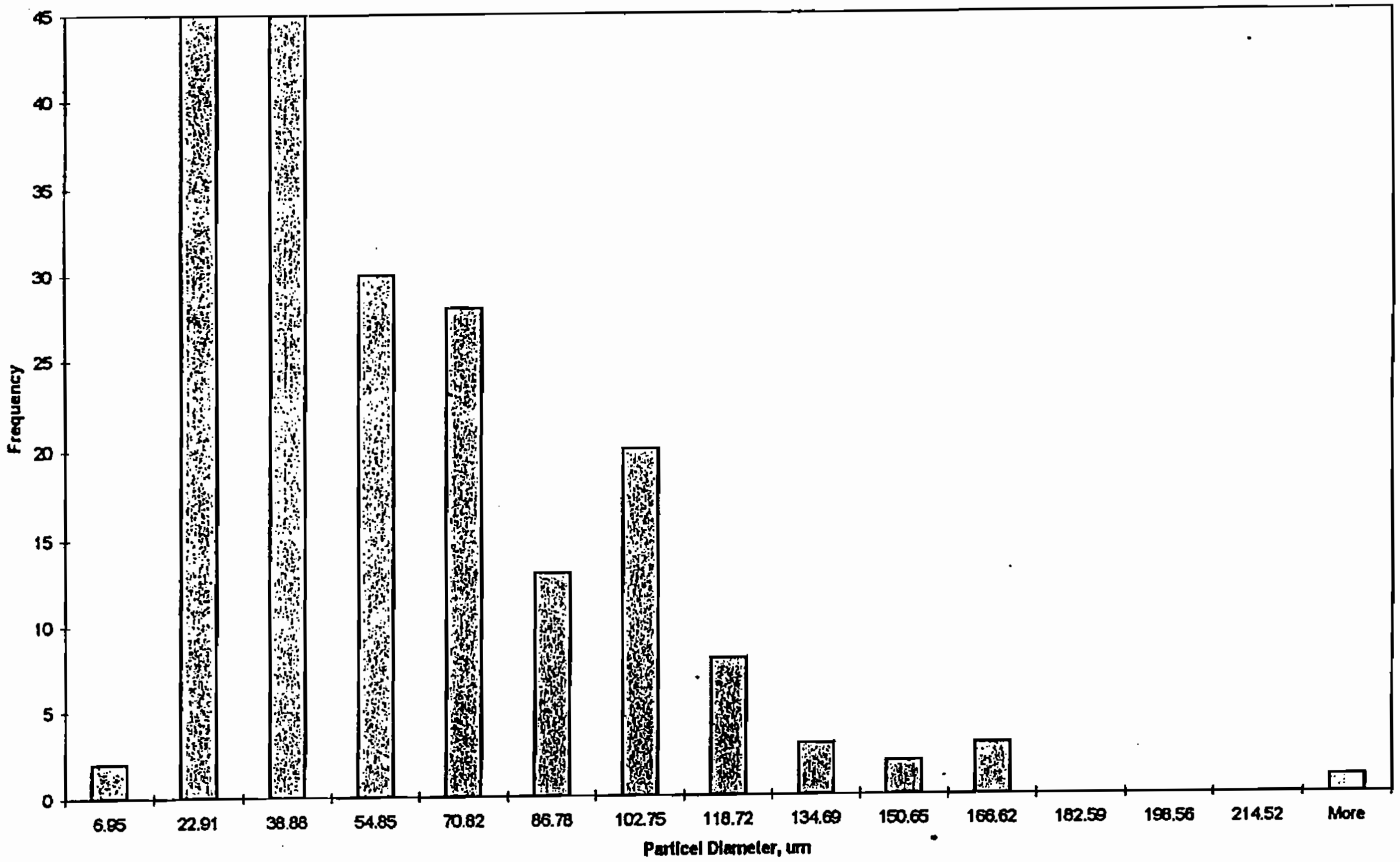
Histogram



ETA ENVIRONMENTAL P/N 28211 SAMPLE 6G40 NEOPRENE GROUND RUBBER PARTICLE SIZE DISTRIBUTION

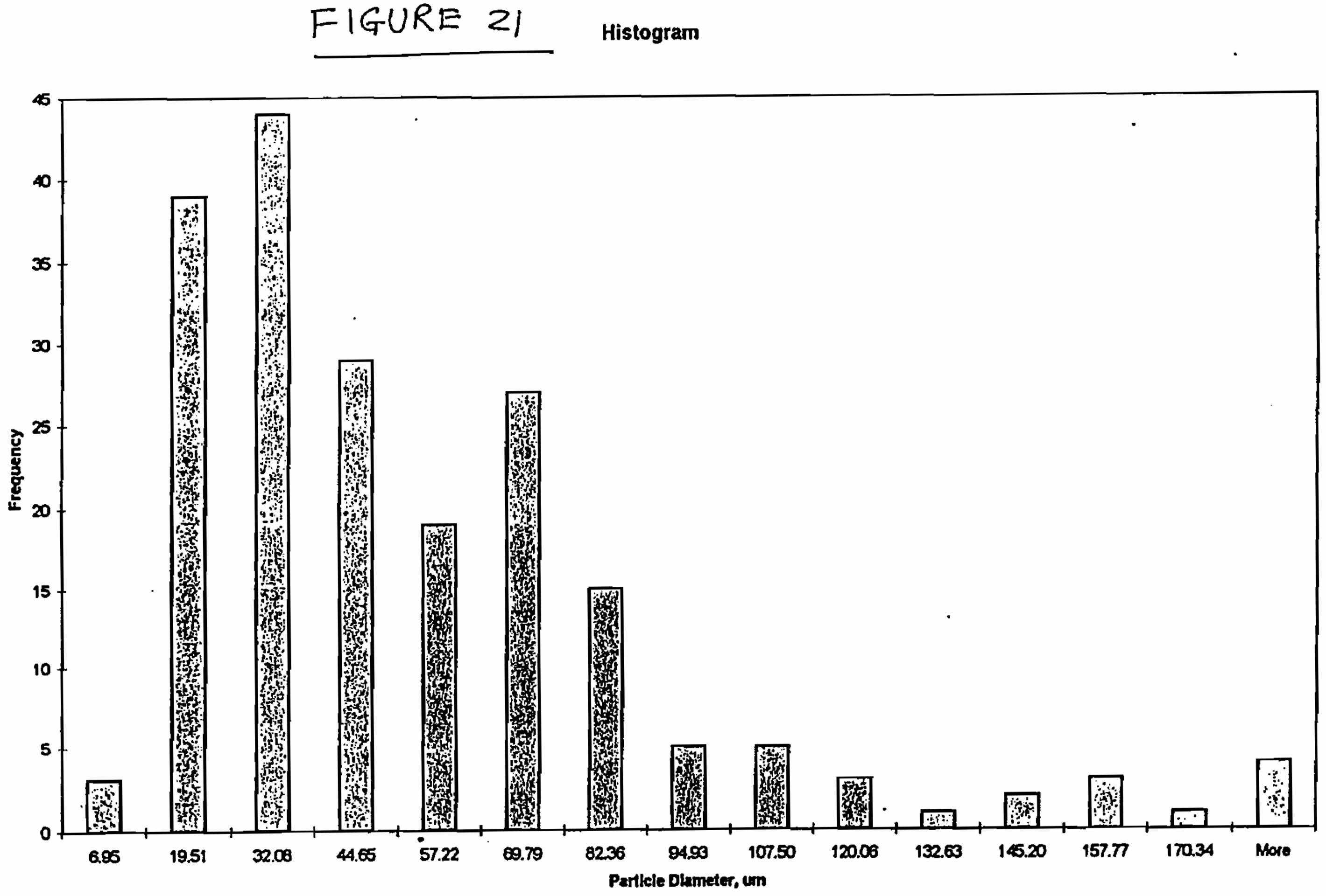
CONTROL

FIGURE 20 Histogram



ETA ENVIRONMENTAL P/N 28211 SAMPLE GR1 NEOPRENE GROUND RUBBER PARTICLE SIZE DISTRIBUTION

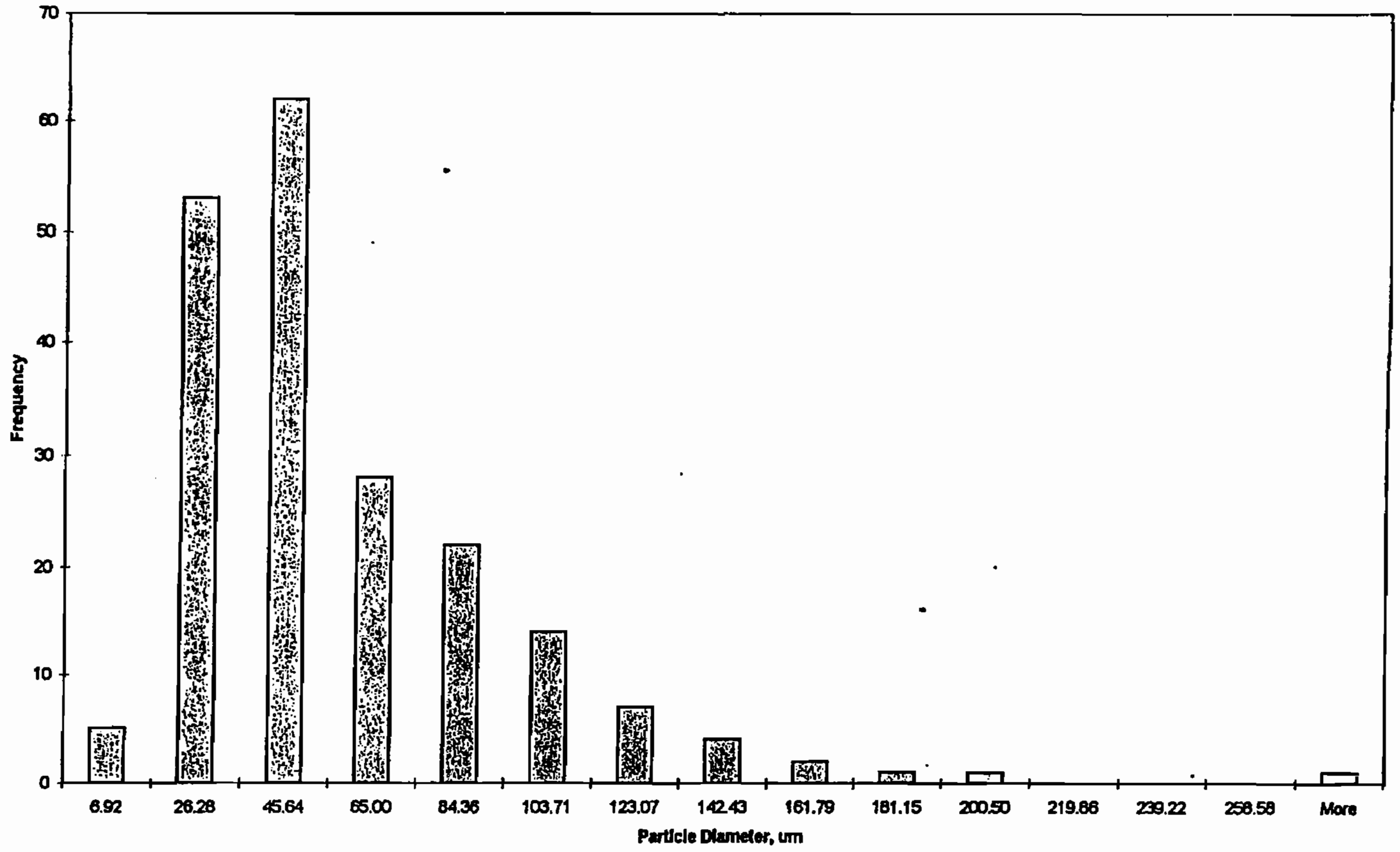
FIGURE 21



ETA ENVIRONMENTAL P/N 28211 SAMPLE GR3 NEOPRENE GROUND RUBBER PARTICLE SIZE DISTRIBUTION

FIGURE 22

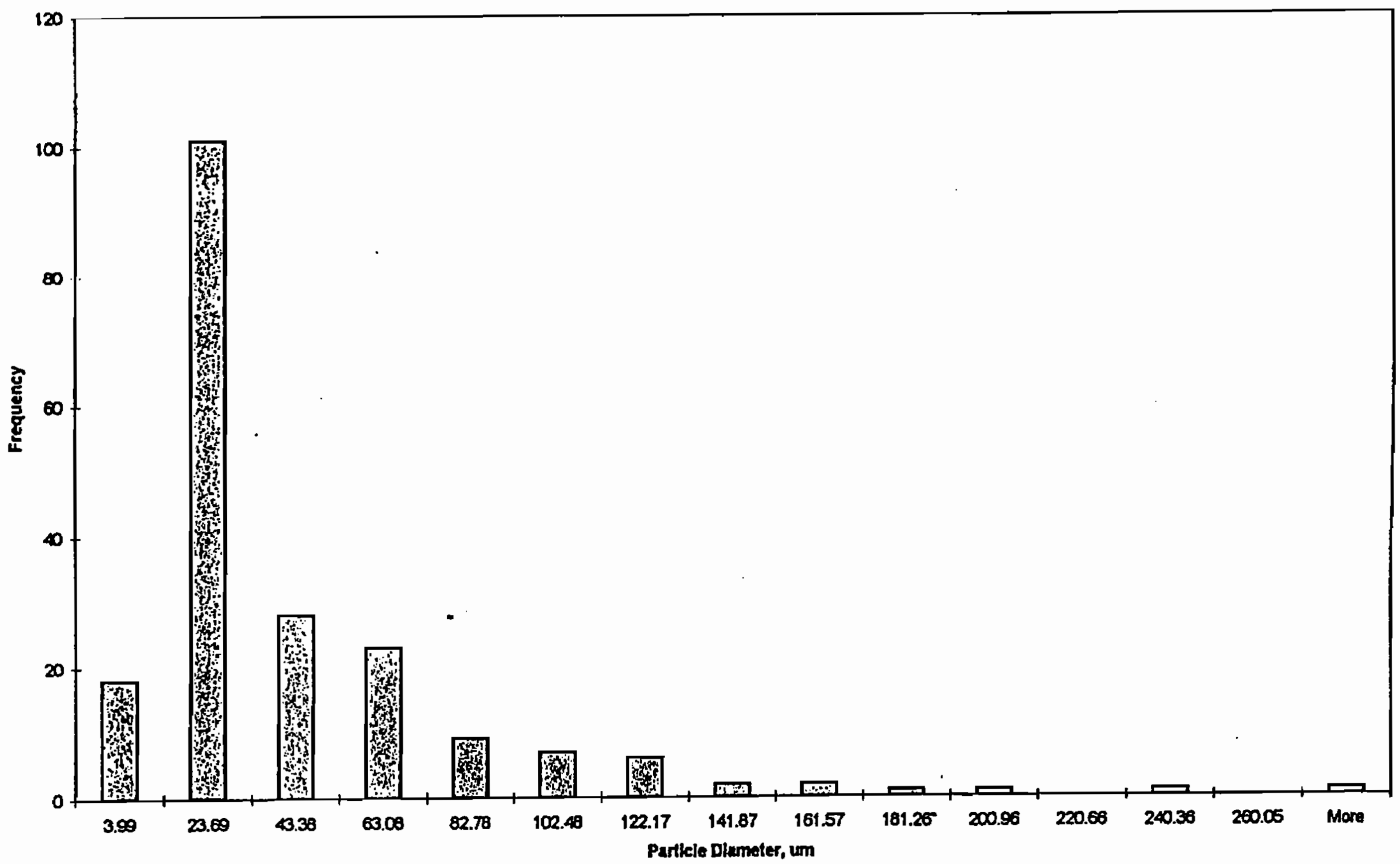
Histogram



ETA ENVIRONMENTAL P/N 28211 SAMPLE GRF NEOPRENE GROUND RUBBER PARTICLE SIZE DISTRIBUTION

FINAL PASS

FIGURE 23 Histogram



We can note three things: One, ultrasonically dispersed particles are separated from each other whereas "as-received" samples show large agglomeration. Secondly, with processing steps, finer particles were produced. Thirdly, even the final-pass sample has few large particles. See Figures 24-27.

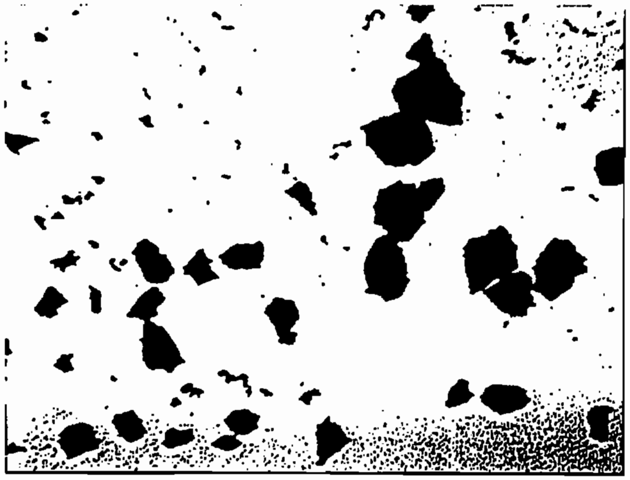
D. DETERMINATION OF CARBON BLACK PARTICLES

The finely ground rubber samples were dispersed in acetone and deposited on a Formvar/carbon coated copper grid.

The dispersed ground rubber samples were analyzed under a transmission electron microscope (TEM),Philips model EM400T. The individual particles were identified and the sizes of only those particles with at least half a diameter visible, measured using Jandel Scientific software (Sigmascan©). The data were transferred to the EXCEL spreadsheet of a window-based PC and respective histograms were obtained.

Only samples 6RF and 2RF were analyzed and no carbon black aggregates or individual particles were observed in the TEM. Therefore, no photomicrographs were taken or are included in this report. Only very large ground rubber particles were seen in the TEM.

Figure 24

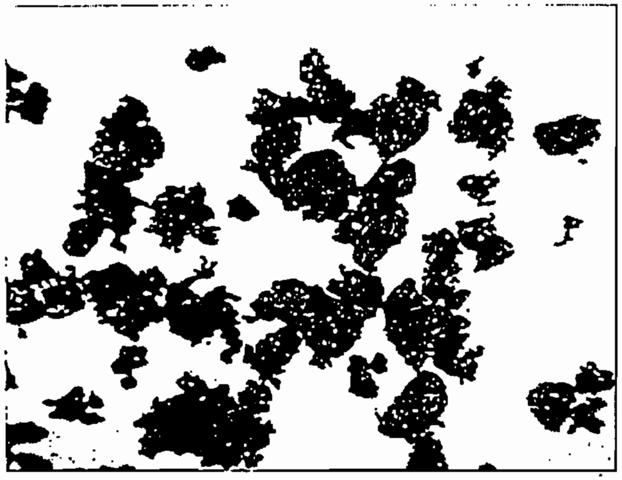

ETA P/N 28211 2G30 20X Transmitted Light [——] 500µm

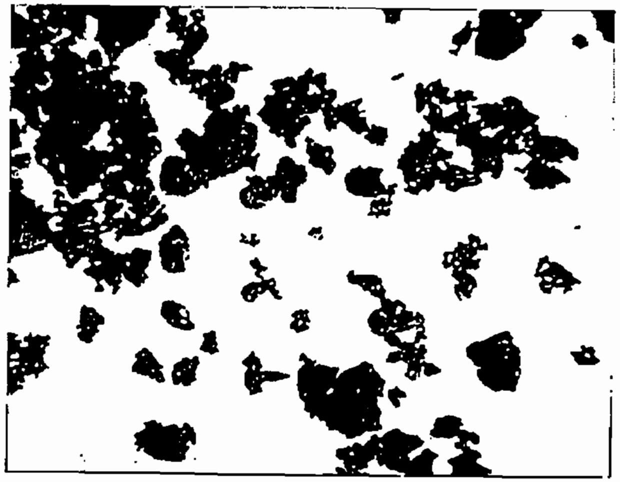

ETA P/N 28211 2G30R1 20X Transmitted Light [——] 500µm

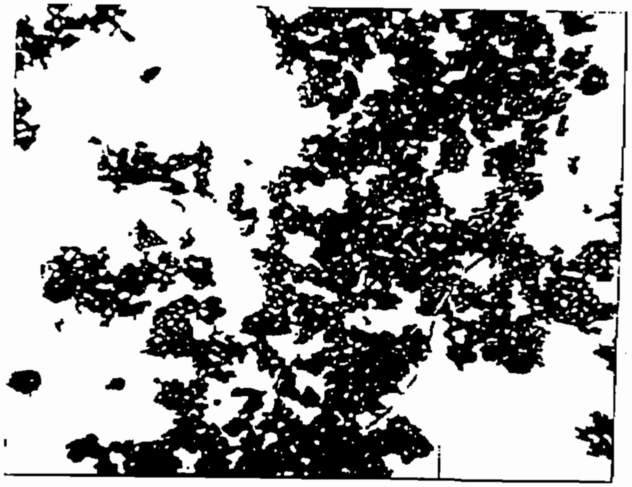

:TA P/N 28211 2R3 20X Transmitted Light [——] 500µm

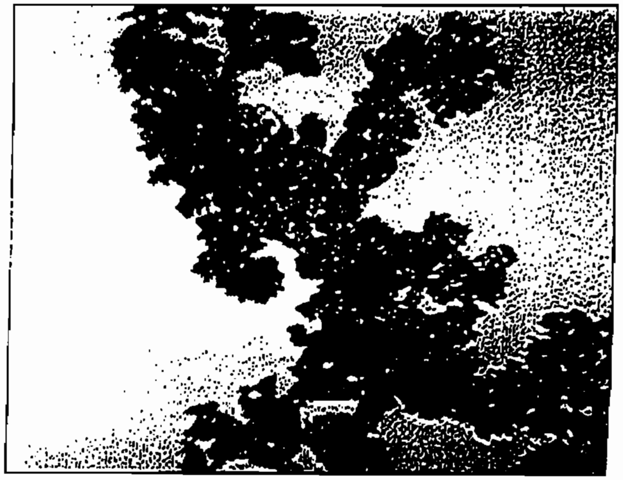

ETA P/N 28211 2RF 20X Transmitted Light [——] 500µm

Fig. 25


ETA P/N 28211 2G30 20X Reflected Light [——] 500µm


ETA P/N 28211 2G30R1 20X Reflected Light [-------] 500µm


ETA P/N 28211 2R3 20X Reflected Light [-------] 500µm

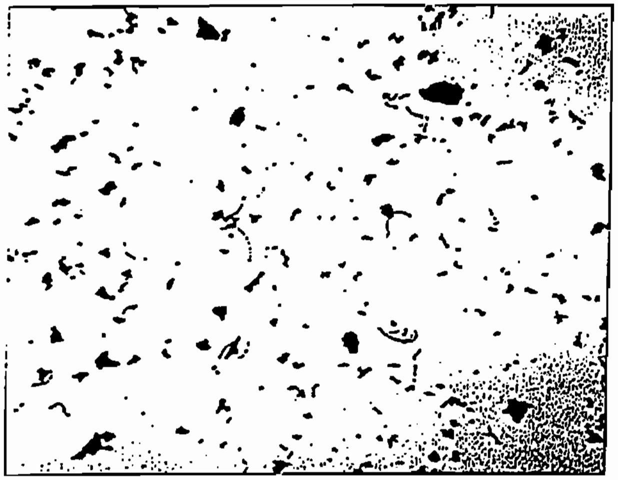

ETA P/N 28211 2RF 20X Reflected Light [-------] 500µm

37

Figure26

ETA P/N 28211 6G40 20X Transmitted Light [——] 500µm

ETA P/N 28211 6R1 20X Transmitted Light [——] 500µm

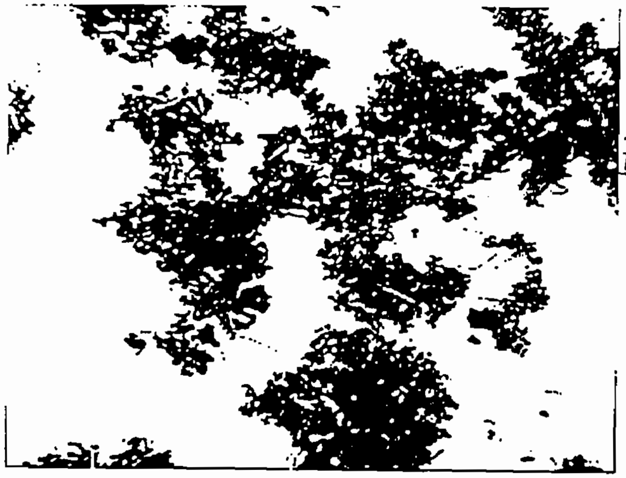


ETA P/N 28211 6R3 20X Transmitted Light [——] 500µm

ETA P/N 28211 6RF 20X Transmitted Light [-------] 500µm

38

Figure 27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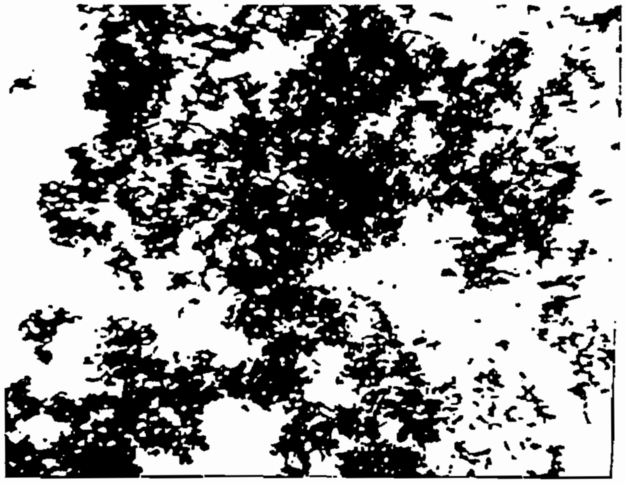
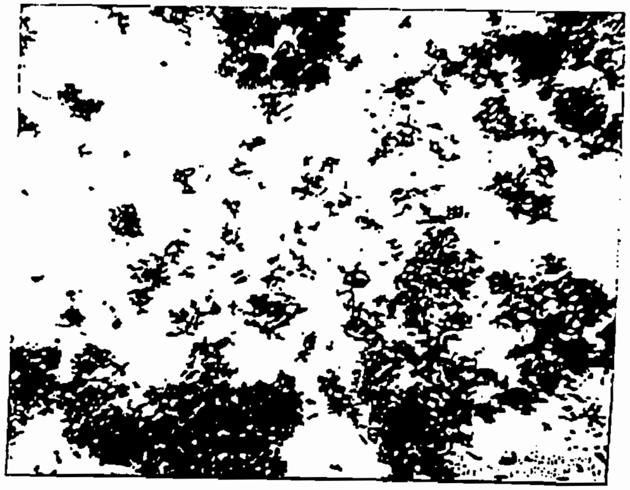
ETA P/N 28211 6R1 20X Reflected Light [-------] 500µm


ETA P/N 28211 6R3 20X Reflected Light [——] 500µm


ETA P/N 28211 6RF 20X Reflected Light [-------] 500µm

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CONCLUSIONS

1. Swelling efficiencies of fresh and recovered solvents were equal for both solvents, cyclohexane (EPDM) and ethyl acetate (neoprene).
2. In general, crosslink density decreased and, hence, degree of devulcanization increased with CRM processing.
3. Percent devulcanization after 5th and final pass for EPDM is about 16%. For neoprene, it is about 43% after the 4th and final pass.
4. Density of all EPDM sheet samples, including the final pass, is the same (about 1.20 gm/cm^3). For neoprene the control compound (cured unground) is higher (1.4 gm/cm^3) than the others which are around 1.3 gm/cm^3.
5. Percent residue is filtered solvent obtained after processing is about 8% for EPDM and for neoprene it is 0.8%.
6. No polymer was detected in residues for EPDM and neoprene either by GPC or FTIR.
7. For EPDM residue, there was no detectable presence (using HPLC) of any sulfur, TMTD or MBTS. These curatives were used in the original compound. This means that these chemicals are staying with the compound. TLC did not detect any methyl fragments of TMTD.
8. For neoprene compound, presence of octamine (antioxidant) and Wingstay 100 (antiozonant) was observed. No curative fragments were detected either by HPLC or TLC.
9. With CRM processing, particles become finer as indicated by the Ro-Tap method and LOM ultrasonic technique. For EPDM final pass sample, most particles are in 4-12 micron range. For the neoprene final pass, most particles are in 4-64 micron range.
10. "As-received" sample showed heavy agglomeration whereas ultrasonic method shows dispersion of individual particles in LOM.
11. Ultramicrotone samples, when examined under TEM, showed no presence of individual carbon black particles. This means that even after final pass black stays attached with polymer chain.

RECOMMENDATIONS

1. Use recovered solvents for swelling ground rubber whenever possible.
2. Work should be extended to determine chemical contents of EPDM and neoprene residues.
3. LOM-ultrasonic examination should be conducted on clay-coated samples obtained in Ro-Tap sieving.
4. Determine any correlation between particle sizes and properties obtained by Dayco and Cooper.
5. A study should be conducted on addition of different amounts of curatives in recipe, with no-addition being the control, in an attempt to compensate of devulcanization during processing.
6. Particle size and particle surface characterization should be done after CRM processing of ambient and cryogenically ground particulates.

REFERENCES

1. Patent 5,677,354 on *Process for Reclaiming Cured or Semi-Cured Rubber* issued to Prof. Lima on October 14, 1997.
2. Paul Standley's trip report "Neoprene Devulcanization Trials @ Relastomers S/A", September 23, 1997.
3. Baranwal's trip report "Catalytic Regeneration of EPDM Compound, ETA 2-G30," an ARDL report, October 15, 1997.

Appendix B
Analysis of Bench-Scale Neoprene and EPDM

"More Than Testing, We Care"

AKRON RUBBER DEVELOPMENT LABORATORY, INC.
2887 Gilchrist Road • Akron, Ohio 44305
1-800-830-ARDL • (330) 794-6600 • FAX (330) 794-6610

PN 28211

Status Report
on
Catalytic Rubber Regeneration

for

Mr. Fernley Smith
ETA, Inc.
3862 The Ridge
Port Clinton, OH 43452

by

Dr. Krishna C. Baranwal

June 14, 1997

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OBJECTIVES

The main objective was to determine the most suitable solvent for each of the four compounds based on natural rubber, EPDM, NBR and neoprene.

LITERATURE SEARCHES

After appropriate published literature searches, reading and reviewing published information, we selected solvents listed in Table I for our study.

Criteria for a good solvent were:

a) Boiling points lower than 85°C (which is the drying temperature for swollen samples).

b) Be compatible with polymers (more or less same solubility parameter as the polymer).

c) Be readily available at a reasonable price.

d) Be environmentally acceptable to work with.

Boiling points and solubility parameters are listed in Table I. Solubility parameters of polymers are given in Table II.

EXPERIMENTAL

Mixing & Curing

Four compounds based on NR, EPDM, NBR and neoprene were mixed in a B-Banbury®. Recipes are listed in Table III. Tom Dendinger of Cooper provided recipes for NR and EPDM compounds. Paul Standley gave recipe for NBR and Jerry Rogers of Dayco furnished recipe for neoprene.

Swelling Measurements

About 10 mm x 30 mm strips of duplicate samples were cut from each cured tensile sheet, weighed and suspended from wires equipped with spacers, to ensure even exposure to the solvent.

The specimens were immersed in the solvent. After one, two, three, four and six hours, duplicate specimens were removed from the solvent and quickly weighed.

The percent weight gain at each time intervals was calculated and the average value obtained from the duplicate specimens was reported. Data are reported in Table V.

TABLE I. Information on Solvents

	Solvents	B.P. (°C)	Solubility Parameter	Other Information
1.	Hexane	69	7.3	
2.	Cyclohexane	81 √	8.2	Sp. Gr. 0.78, see attached MSDS
3.	Heptane	98	7.4	
4.	Ethyl Acetate	76-77.5	9.1	
5.	MEK	80	9.3	
6.	Cyclohexanone	111	9.7	
7.	THF	66	9.5	Sp. GR. 0.89, see attached MSDS
8.	Diacetone Alcohol	166	9.2	
9.	50/50 Ethyl Acetate/ Heptane	76-98	--	

TABLE II.
Solubility Parameter Ranges of Polymers

Polymer	Solubility Parameters
Natural Rubber	8.0 - 8.5
EPDM	7.5 - 8.6
NBR	8.7 - 9.3
Neoprene	8.1 - 9.4

TABLE III. Compounding Formulations

S.N.	Compound No. → Ingredient ↓	NR ETA-1	EPDM ETA-2	ETA-3	ETA-4
1.	Natural Rubber	100.0	--	--	--
2.	Neoprene GRT	--	--	--	100.0
3.	Zinc Oxide	5.0	5.0	5.0	5.0
4.	Stearic Acid	1.0	1.0	1.0	2.0
5.	N-774	43.0	--	100.0	--
6.	Ag. Resin D	2.0	--	--	--
7.	6 PPD	2.0	--	--	--
8.	Wax	2.0	--	--	--
9.	Aromatic Oil	2.0	--	--	--
10.	Sulfur	1.5	2.0	0.75	--
11.	TBBS	2.0	--	--	--
12.	TMTD	0.2	3.0	--	--
13.	Keltan P597 (EPDM)	--	74.0	--	--
14.	Keltan 5508 (EPDM)	--	63.0	--	--
15.	N-650	--	200.0	--	--
16.	Whiting	--	51.0	--	--
17.	Paraffin Oil	--	123.0	--	--
18.	Cal. Oxide	--	8.0	--	--
19.	MBTS	--	1.5	--	0.75
20.	Paracil BLT (Nitrile)	--	--	100.0	--
21.	TP-95 Plasticizer	--	--	15.0	--
22.	Paraplex G-25 Plasticizer	--	--	5.0	--
23.	AMINOX	--	--	1.5	--
24.	TMTM	--	--	1.5	--
25.	Phthalic Anhydride Retarder	--	--	0.5	--
26.	MgO	--	--	--	4.0
27.	Dioctylated Diphenyl Amine	--	--	--	2.0
28.	N-762	--	--	--	60.0
29.	Aromatic Oil Type 102	--	--	--	6.0
	TOTALS	160.7	531.5	230.25	179.75

56°C — "24" vacuum"

or 50°C - 27"

Rheometer data and tensile sheet cure times are given in Table IV.

TABLE IV. Rheometer Data and Tensile Sheet Cure Times

Cmpd. No.	Polymer	Cure Temp (°F), for Rheometer & Tensile Slabs	Rheometer Data				Cure Times for Tensile Sheets (min)
			Min Torque (in-lb)	Max Torque (in-lb)	t_s (min)	t_{90} (min)	
ETA-1	NR	285	9.7	36.6	6.0	9.1	15
ETA-2	EPDM	340	5.3	22.6	2.5	6.9	15
ETA-3	NBR	340	10.8	34.8	2.5	5.0	10
ETA-4	Neoprene	340	5.7	37.7	1.7	11.6	20

TABLE V. Swelling Data for Cured Compounds

Compound	Solvent	Immersion Time (hrs)	% Weight Increase
ETA-1 (NR)	Hexane	1	55.4
		2	72.3
		3	77.5
		4	78.4
		6	77.1
	Cyclohexane	1	58.1
		2	93.3
		3	115.8
		4	130.3
		6	139.2
	Heptane	1	48.1
		2	69.3
		3	75.7
		4	78.9
		6	79.7

TABLE V. Swelling Data for Cured Compounds

Compound	Solvent	Immersion Time (hrs)	% Weight Increase
ETA-2 (EPDM)	Hexane	1	39.9
		2	32.6
		3	27.5
		4	25.5
		6	24.1
	Cyclohexane	1	48.7
		2	70.2
		3	68.6
		4	65.0
		6	59.0
	Heptane	1	44.5
		2	38.8
		3	33.4
		4	30.6
		6	28.3
ETA-3 (NBR)	Ethyl Acetate	1	48.4
		2	74.3
		3	85.9
		4	89.4
		6	91.9
	Methyl Ethyl Ketone	1	78.3
		2	103.2
		3	110.5
		4	111.8
		6	111.3
	Tetrahydrofuran	1	115.9
		2	153.8
		3	160.8
		4	162.4
		6	162.7
	Cyclohexanone	1	35.5
		2	58.7
		3	75.6
		4	98.5
		6	132.2
	Diacetone Alcohol	1	9.9
		2	14.5
		3	18.5
		4	23.2
		6	29.4

TABLE V. Swelling Data for Cured Compounds

Compound	Solvent	Immersion Time (hrs)	% Weight Increase
ETA-4 (Neoprene)	Ethyl Acetate	1	21.4
		2	31.5
		3	38.6
		4	41.7
		6	43.8
	Methyl Ethyl Ketone	1	26.2
		2	39.0
		3	45.1
		4	47.1
		6	47.9
	Tetrahydrofuran	1	98.7
		2	133.9
		3	144.0
		4	145.8
		6	144.6
	Ethyl Acetate/Heptane, 50/50	1	26.0
		2	39.4
		3	46.5
		4	49.3
		6	50.0
	Cyclohexanone	1	25.7
		2	40.1
		3	54.1
		4	66.6
		6	89.9

Data are also plotted in Figures 1-4.

Drying of Samples

We also dried swollen samples at 85°C in a vacuum oven to determine optimum drying times. Data are listed in Table VI and plotted in Figures 5-8. It appears that swollen samples are completely dry in 4 hours for NR, 1 hour for EPDM and 3 hours for NBR and Neoprene.

TABLE VI. Drying of Swollen Samples at 85°C in Vacuum

.015 Thickness

Polymer	Solvent	Piece Orig Dry Wt (gms)	WEIGHT IN GRAMS AFTER DRYING FOR								
			0 Min.	15 Min.	30 Min.	45 Min.	60 Min.	90 Min.	150 Min.	210 Min.	270 Min.
NR	Hexane	1.5170	2.7060	1.8086	1.5812	1.4959	1.4630	1.4380	1.4224	1.4180	1.4168
	Cyclohexane	1.5465	3.7580	2.2257	1.7811	1.6186	1.5445	1.4880	1.4537	1.4454	1.4421
	Heptane	1.4611	2.6248	1.7391	1.5076	1.4302	1.3981	1.3763	1.3663	1.3644	--
EPDM	Hexane	1.5111	1.8960	1.1228	1.0587	1.0550	1.0548	1.0545	1.0541	--	--
	Cyclohexane	1.5376	2.3750	1.2867	1.1107	1.0772	1.0726	1.0713	1.0711	--	--
	Heptane	1.6764	2.1566	1.2610	1.1757	1.1698	1.1694	1.1693	--	--	--
NBR	THF	1.7031	4.4000	2.2596	1.8168	1.6816	1.6220	1.5752	1.5398	1.5255	1.5168
	Cyclohexanone	1.7110	4.5252	3.4463	2.7907	2.4280	2.1800	1.9272	1.7258	1.6530	1.6130
CR	THF	1.9257	4.7200	2.5141	2.0728	1.9313	1.8674	1.8168	1.7807	1.7669	1.7597
	Cyclohexanone	1.9613	4.5059	3.4270	2.8991	2.5969	2.3845	2.1624	1.9830	1.9133	1.8756

CONCLUSIONS

Based on the swelling data, we conclude the following:

TABLE VII. Swelling & Drying Times for Recommended Sovlents

Compound	Best Solvent (from the list of solvents used)	Optimum Swelling Time (hrs) (Approx)	Optimum Drying Time at 85°C Under Vacuum (hrs)
NR	Cyclohexane	4-6	4
EPDM	Cyclohexane	3	1
NBR	THF	3	3
Neoprene	THF	3	3

RECOMMENDATIONS

I recommend that solvents, swelling and drying times listed in Table VII be used for pilot plant runs.

Krishna C. Baranwal, Ph.D.
Executive Vice President - Technical

mas·PN28211ETA.kcb

Fig. 1 **SOLVENT SWELL OF RUBBER** PN 28211

COMPOUNDED NR (ETA-1)

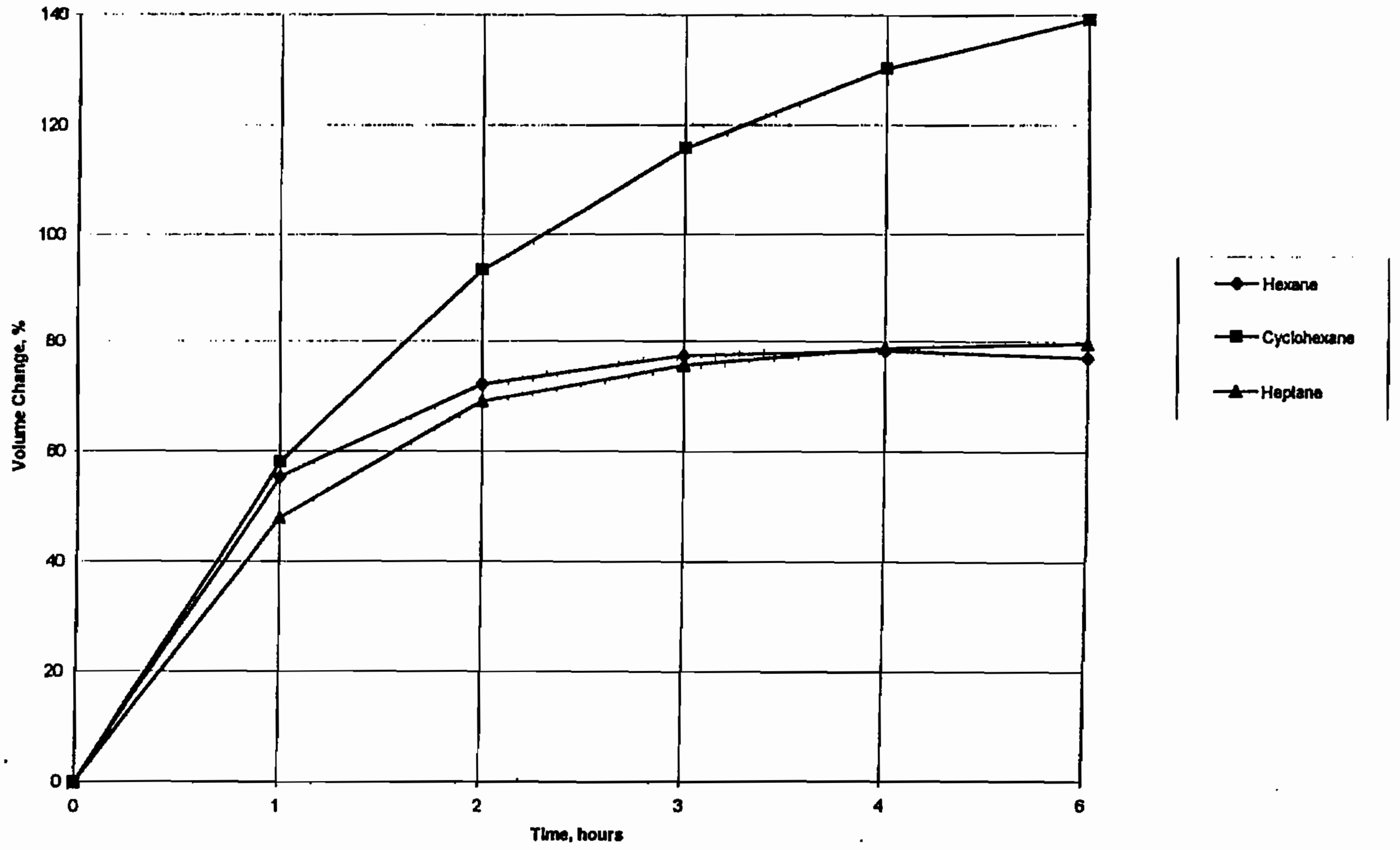


Fig. 2 **SOLVENT SWELL OF RUBBER**

Compounded EPDM (ETA-2)

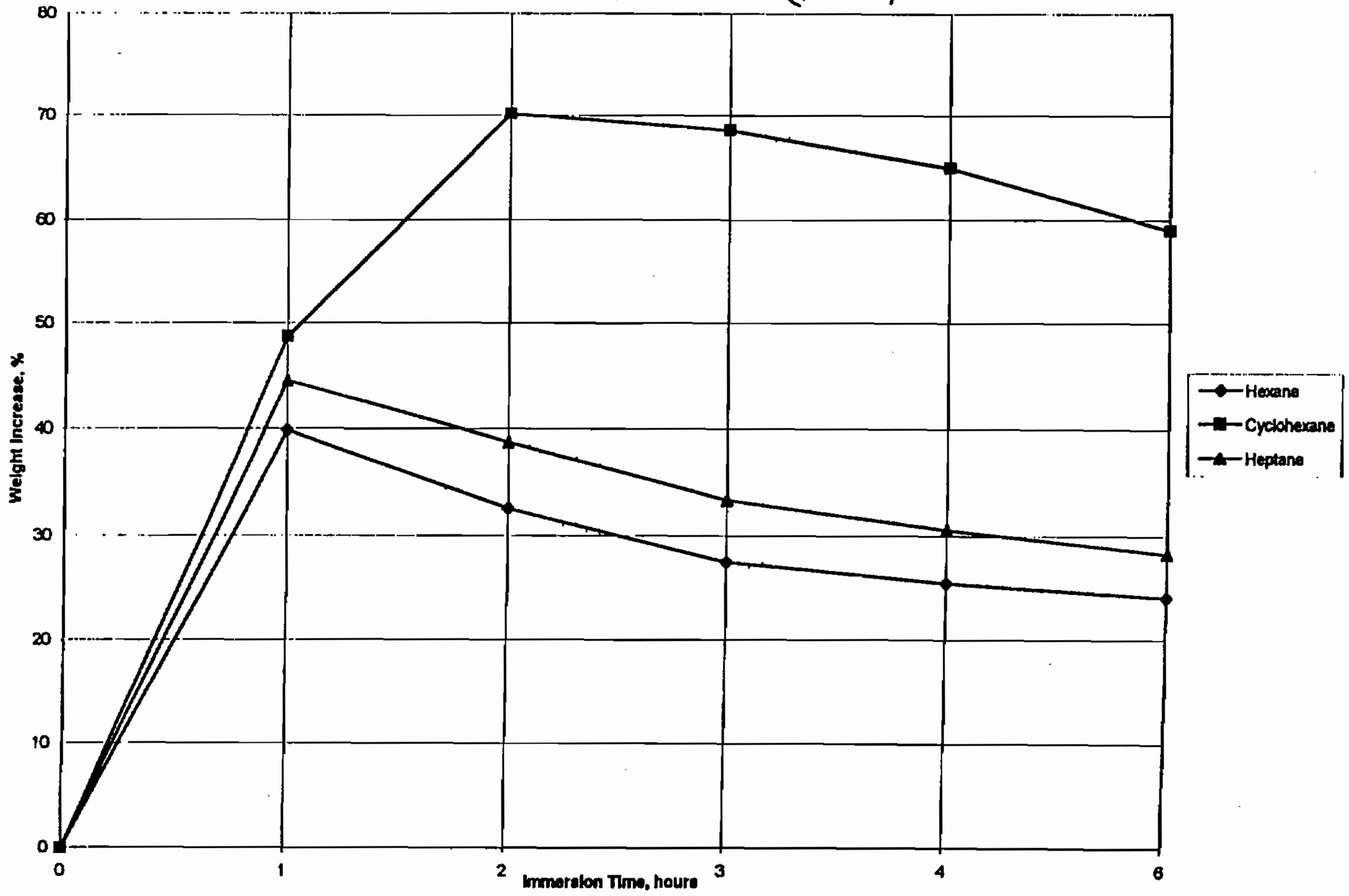
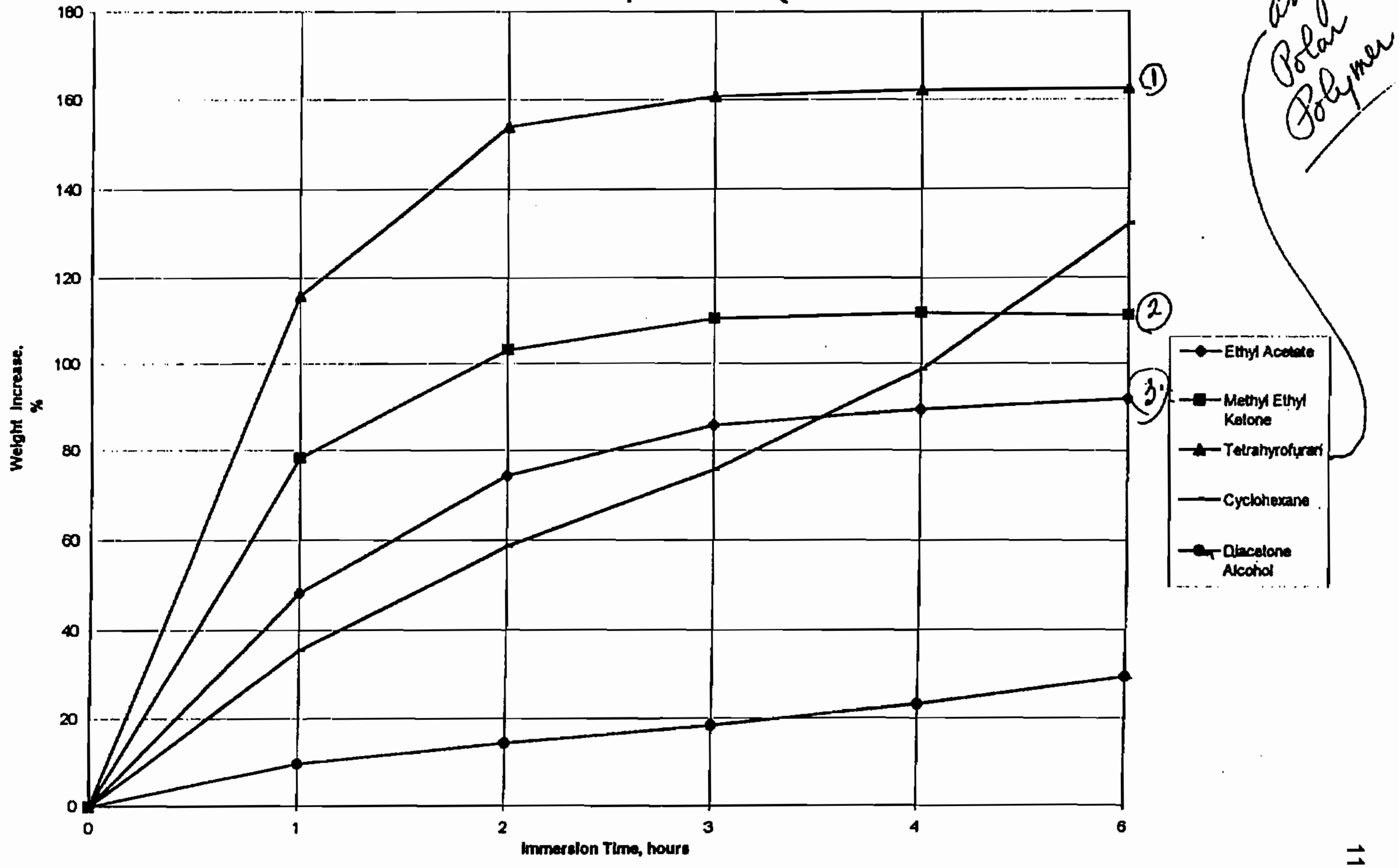


Fig. 3 SOLVENT SWELL OF RUBBER

Compounded NBR (ETA-3)



use with any Polar Polymer

Fig. 4 SOLVENT SWELL OF RUBBER

Compounded CR (ETA-4)

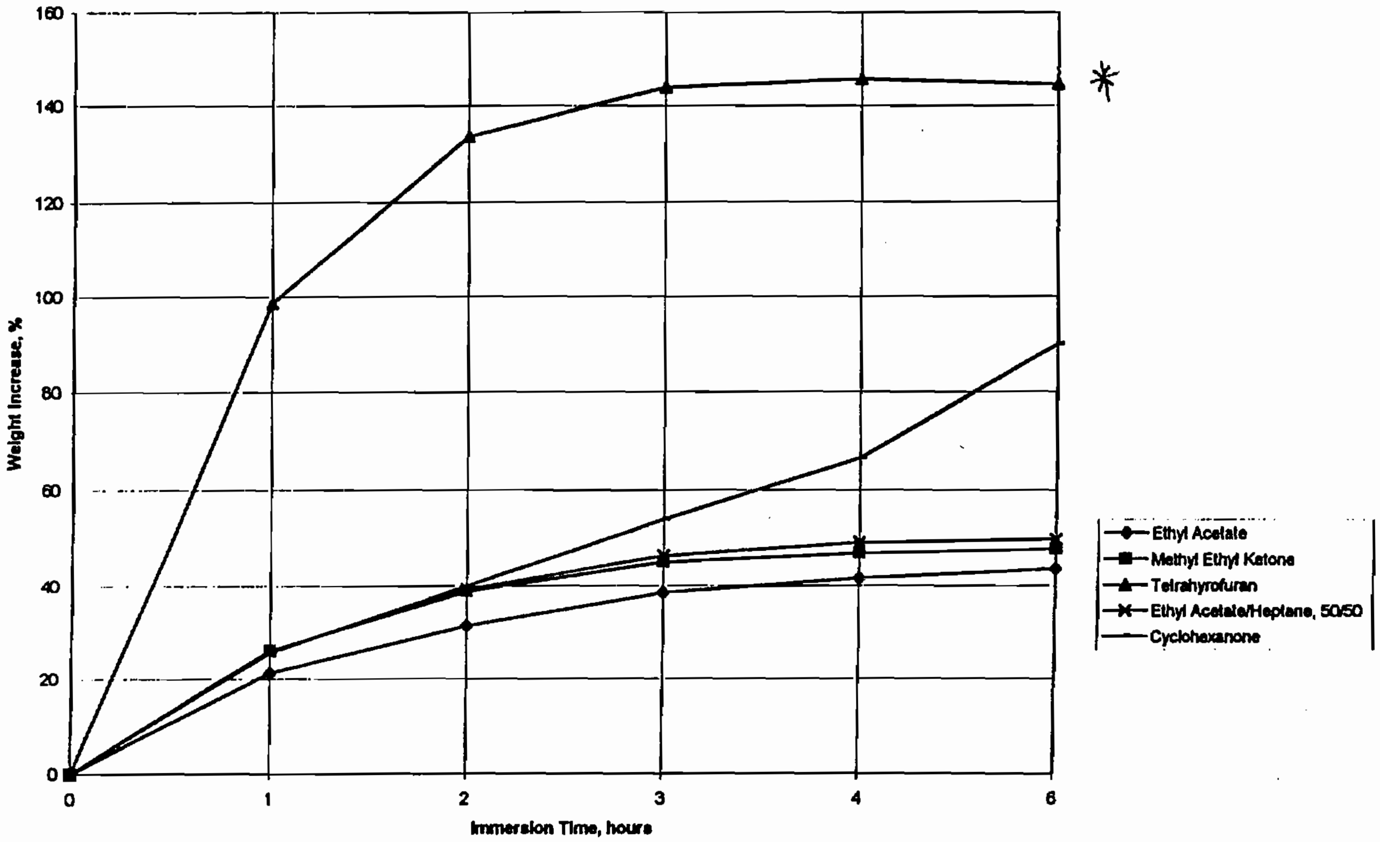
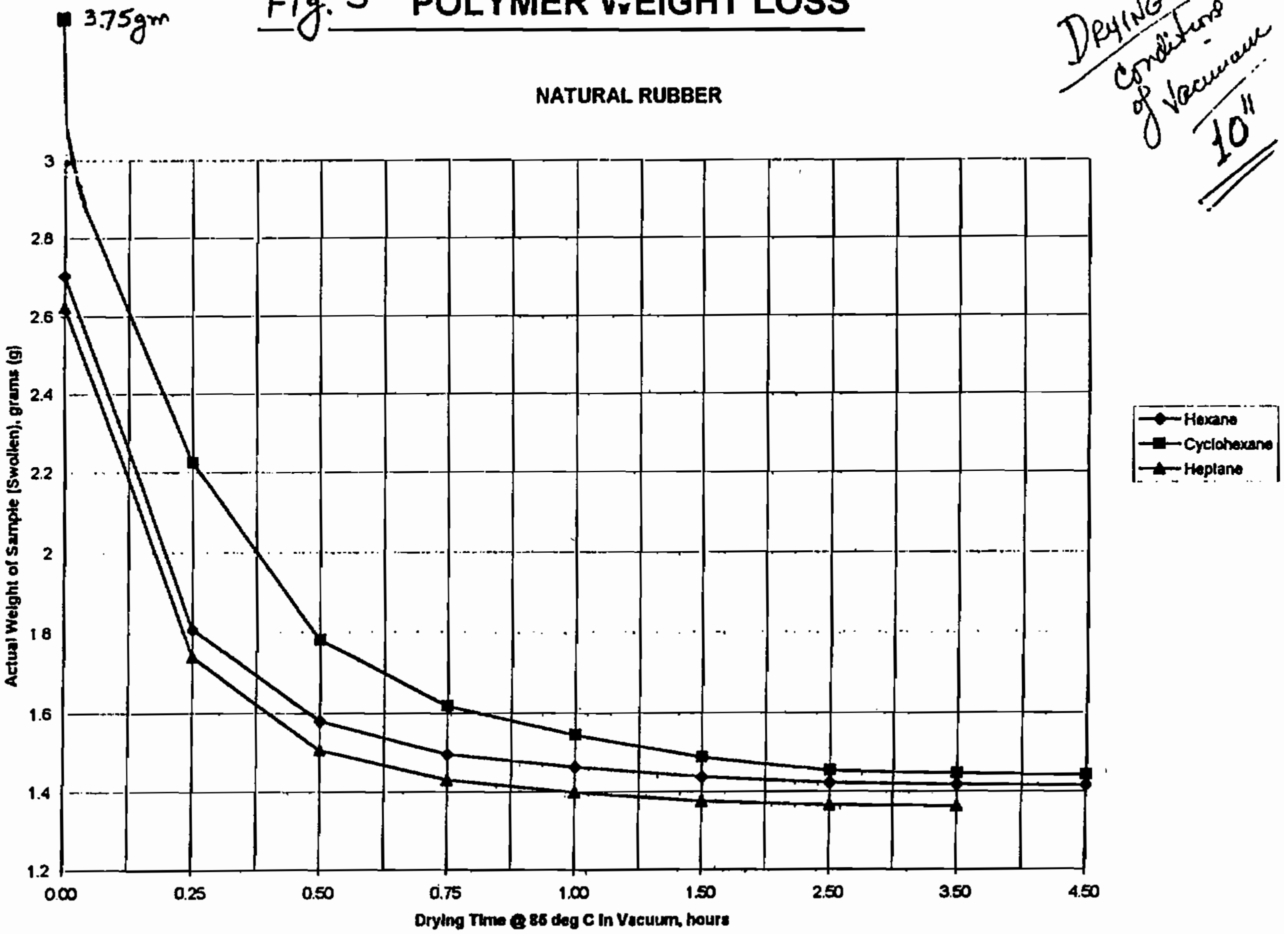


Fig. 5 POLYMER WEIGHT LOSS



Drying Conditions of Vacuum - 10"

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Fig. 6 POLYMER WEIGHT LOSS

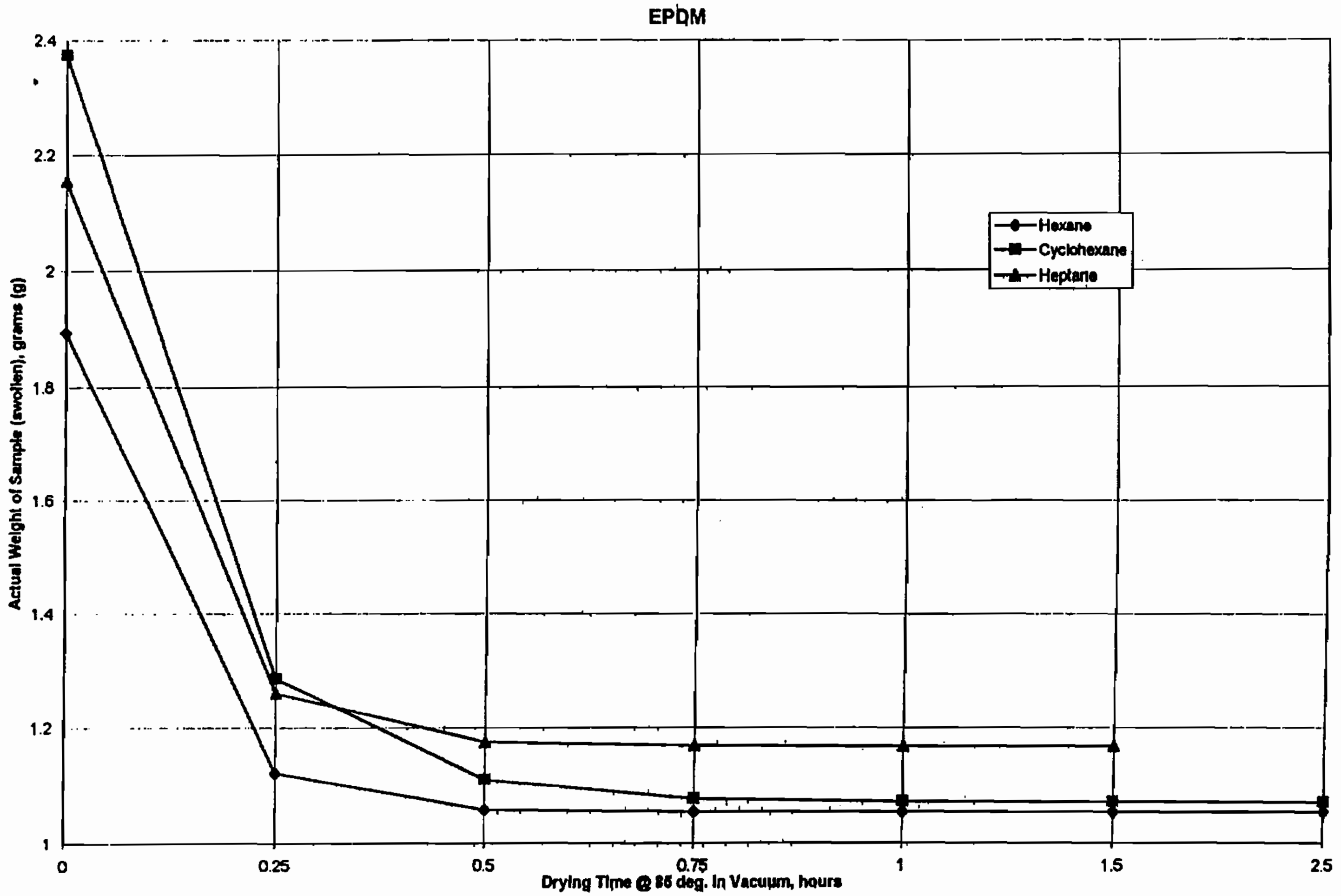

Fig. 7 POLYMER WEIGHT LOSS

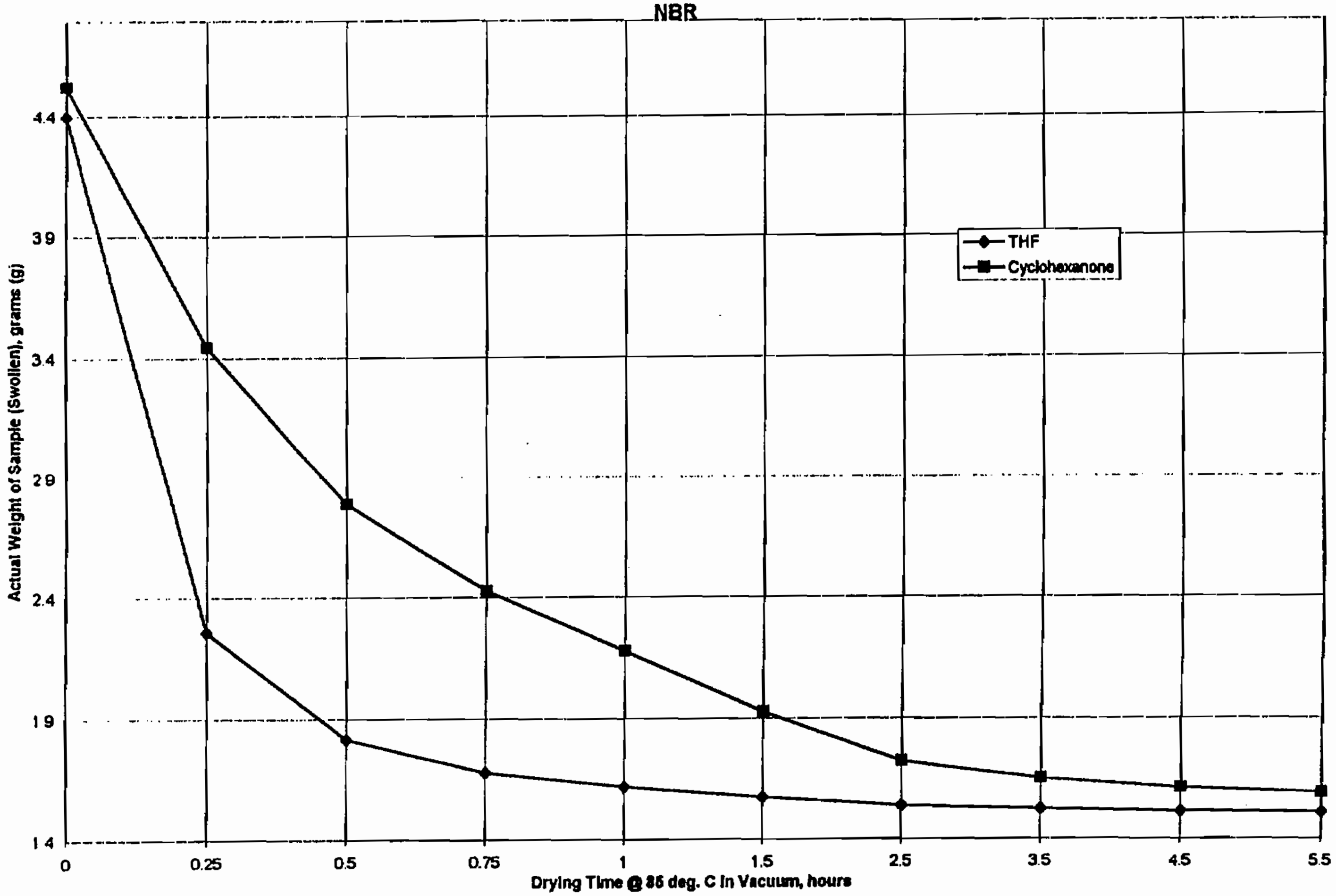

Fig. 8 POLYMER WEIGHT LOSS

CR