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SUMMARY

The use of methanol in combination with gasoline as a motor fuel can lead to a reduced need for crude oil imports. Previous experience with ethanol suggests that there will be material compatibility problems associated with the use of methanol in existing automotive fuel systems. An investigation was initiated to determine reasonable precautions that might be taken to potentially minimize risks of operating motor vehicles on methanol-gasoline in the Department of Energy's fleet test program on alcohol-gasoline blends. This project was conducted to seek out currently available fuel additives that would decrease the severity of methanol attack on fuel system materials.

Thirteen additives, sold for the most part as corrosion inhibitors for application in various types of liquid handling systems, were offered by suppliers as having potential for use as corrosion inhibitors in methanol-gasoline fuel blends. These additives were not expected to have any effect on nonmetals. Six of these additives having a diversity of applications and chemical types were chosen for evaluation, and to protect their proprietary nature, were designated A, B, C, D, E and F.

These additives were tested in a typical gasoline and test blends containing 2.5, 5.0, 10.0, and 20.0 volume percent methanol, with 2-butanol as cosolvent and water. Solution corrosivity tests were conducted with 10 metals at 43°C for a 30-day period. Compatibility tests were made on 12 nonmetals (6 elastomers, 5 plastics and cork) at 24°C over a 72-hour exposure period. Changes were determined in the properties of tensile strength, ultimate elongation, dimensional change and hardness. Methanol concentrations were changed to 5, 7.5 and 10 volume percent for testing in Phase II with the five metals showing corrosion and zinc, which was not affected. The number of polymeric materials was reduced to six.

None of the fuel blends tested in Phase I with and without additives had any corrosive effects over an extended test period on aluminum, zinc, carbon steel, stainless steel and cast iron. None of the metals underwent any weight change attributable to corrosivity effects and only bronze had any detectable pitting. Although light, the pitting was the only effect on the bronze which could be used to determine corrosivity effects. Only color changes were noted on brass, copper and terneplate, and the coloration was assumed to be a corrosion related change. In the blends containing 20 percent methanol, magnesium was severely corroded by the vapor phase, and with the exception of the additive D test,

disintegrated after the suspension point failed and the test coupon fell into the test solution. The test blends containing lower concentrations of methanol had no effect on the immersed part of the magnesium specimens but discolored the metal where it was in contact with the vapors.

The nonmetals were tested in the same control and test blends as the metals. Changes in the physical properties were determined before and after immersion in the test blends to determine the effects of the fuels and additives. As expected from information provided by the additive suppliers, only time and concentration dependent effects of methanol were detected on the nonmetals. The additives did not change the deleterious effects of the methanol or otherwise have any effects of their own in the Phase I tests.

Only two additives, B and D, indicated a decrease in the corrosivity of methanol toward brass and bronze and additive E toward terneplate in Phase I tests. Tests were conducted in Phase II with these additives to confirm their apparently protective effects and to determine the effects of combining the additives and of increasing their concentrations.

The results of the Phase II testing repeated well for additive D, the control from Phase I. Additive B seemed to repeat but the results were more sporadic and additive E repeated very well. Additives B and D provided some protection for brass, copper and terneplate, and additive E seemed to increase the corrosion of magnesium and not affect the others. The most corrosivity protection was provided by B and D in combination for brass and copper and possibly for terneplate. The combination of additive E with additive D apparently enhances protection for copper, the only case of E contributing to protection.

The results of Phase II testing of the nonmetals duplicated very closely the Phase I results. The deleterious effect of methanol on these materials was confirmed. The additives, both singly and in combination neither provided any protection for the nonmetals nor had any deleterious effects of their own.

The main objective of the program, to identify and screen commercial additives which might be useful for the protection of materials from the effects of contact with methanol in gasoline fuel blends, was attained. However, further testing under actual application conditions is required prior to use.

INTRODUCTION

Methanol produced from coal has the potential of becoming a major item in this country's alternative fuels inventory. The reduction of crude oil imports and the possible improvement of gasoline octane number constitute the main incentives for using methanol in gasoline motor fuels. However, some technical problems have arisen, among them being those associated with corrosion of metal engine parts and deleterious effects on polymeric materials used in automotive fuel systems.

In new vehicles it may be possible to use improved materials that are not subject to attack by methanol-gasoline, but it is still necessary to seek protection for existing systems. An attractive approach for overcoming these material compatibility problems is the use of currently available commercial fuel additives. A mixture of methanol and tertiary butanol containing a corrosion inhibitor has been developed for use with unleaded gasoline in blends which must meet the EPA legal limit for oxygen content. Concern arises over possibly greater compatibility problems should a waiver request for an increase in oxygen content be granted. Knowledge of the material effects of blends containing higher methanol concentrations is incomplete.

The effects of higher oxygen content on fuel system materials and other related methanol applications questions may be investigated under the planning base provided by the Department of Energy's Alternative Fuels Utilization Program (AFUP). This program provides a planning base for investigating the effects of higher oxygen content on fuel system materials and other related methanol applications questions.(1,2)* As a part of this activity, data are collected on the operation of commercial fleet vehicles with alcohol-gasoline blends. It would be desirable to use an anticorrosion additive, if one were found to be effective, to mitigate problems arising from the use of methanol-gasoline fuel blends.

The project was organized into two main parts: Phase I, the screening phase in which six additives were obtained and evaluated, followed by Phase II, the optimization phase in which three additives exhibiting some apparent protective effects were further evaluated. The main objective of this program was to identify, obtain and evaluate commercially available fuel additives that would be useful for the reduction or elimination of engine and fuel system material deterioration in methanol fuel blends. The six-month technical effort was conducted during the term 10 May 1982 to 10 November 1982.

The materials tested in the program were chosen by NASA and DOE personnel based on information from ARCO's Clean Air Act waiver request for Oxinol,(3) a mixture of methanol and tertiary butanol, as a blending

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*Numbers in parentheses designate references at end of report.

component for gasoline. The materials chosen are representative of those found in automotive fuel systems and were exposed to various conditions and degrees of contact with the fuel. Ten metals consisting of both pure metals and alloys were used for the determination of solution corrosivity effects. The effects of methanol on the twelve nonmetals consisting of elastomers, plastics and a naturally occurring material were known but the effects of additives were not.

This project was not intended to be a comprehensive study of the effects of additives on material compatibilities in methanol-gasoline fuel systems. The intent was to provide information that would be helpful in the choice of materials for these applications and an indication of the potential of additives for lessening the effects of material incompatibilities.

EXPERIMENTAL PROGRAM

The program was divided into six 30-day periods during which two of those periods were required for metal corrosivity determinations. The corrosivity determinations of Phase I and Phase II were conducted during the second and fifth periods, respectively, of the project. The materials compatibility determinations required five to six days for exposure and testing and were conducted during the corrosivity test periods. The remainder of the time was used to acquire blending components and materials; prepare test specimens, fuel blends, and testing equipment; and to evaluate and report results.

Sixteen suppliers of fuel additives were initially contacted in search of corrosion inhibitors that might be applicable to use in methanol-gasoline blends. The suppliers were requested to recommend candidate materials and provide any available technical information since it was desired to encompass as broad a range of applications and chemical types as possible. Ten of the suppliers proposed 13 corrosion inhibitors -two of them experimental-for which they would provide formulating instructions, cost, and any technical information not of a proprietary nature. In consultation with the Project Manager and guided by the available technical information, the six additives described in Table I were chosen. The suppliers indicated some of the additives had been tested and exhibited some potential for corrosivity protection in solutions containing alcohol. Only the results of testing additive C in ethanol mixtures were provided. This additive apparently protected steel and zinc and to a lesser extent terneplate in 20 percent ethanol-gasoline. Brass and aluminum were not affected by the fuel. Since "methanol is more corrosive than ethanol" the supplier's representative recommended a higher concentration of additive C for the methanol studies.

According to the supplier, additive B protects a metal in contact with a petroleum fluid by forming "a thin, tenacious film" which prevents contact of the metal surface with oxygen and water. The technical information provided indicated that all of the additives would be highly immiscible with water.

The suppliers' information indicated none of the additives could be expected to prevent or decrease incompatibilities between fuels and the nonmetals used in fuel systems. The technical information provided suggested that the one thing that could be expected was that the additives themselves would not harm the nonmetals or that they would not worsen the deleterious effects of the fuel blends.

TABLE I. DESCRIPTION OF ADDITIVES CHOSEN FOR TESTING

Test Code	Inhibition Type	Chemical Type	Recommended Concentration, lb/TBL*
A	Corrosion	Organic acid	5
B	Rust in fuels and lubricants	Acylated amines in aromatic hydrocarbons	3
C	Corrosion in ethanol-gasoline fuels	Organic acid	100
D	Corrosion	Substituted high molecular weight succinic acid	2 X vol% methanol
E	Rust and anti-icing in petroleum fuels	Organic acid	15
F	Rust in circulating oils	Fatty acid amide	1,936

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*Pounds per thousand barrels

The conversion factor used for making the fuel blends in the laboratory was 2.853 mg/L, the equivalent of 1 pound per thousand barrels. To determine the amount of additive required for any solution, it was only necessary to multiply the conversion factor by the recommended concentration in pounds per thousand barrels and the desired volume of solution in liters. A solution was made of each additive in gasoline containing the indicated additive in twice the concentration shown in Table I. In this way, the test solutions could be made by a simple one-to-one dilution with the appropriate fluids mixture.

Methanol concentrations of 2.5, 5, 10 and 20 percent (vol) in gasoline were required for the initial series of tests. Methanol-gasoline blends were not expected to exhibit highly corrosive effects on most metals under the proposed test conditions. The broad range of methanol concentrations was chosen in order to make it more likely that some observable effects would be induced.

Three additives, B, D and E were tested in Phase II at three methanol concentration levels, 5, 7.5 and 10 percent (vol). The additive solutions in gasoline were made as before in appropriate multiples of the desired final concentrations. As before, the test solutions for Phase II could be made by making simple dilutions of the additive solutions.

Two 55-gallon drums of typical South Texas gasoline were acquired from a Gulf Coast refinery. The gasoline blending component contained only antioxidant and metal deactivator additives and its properties are shown in Table II. Technical grade methanol of 99.9 percent purity contained traces of acetone and formaldehyde and 0.05 percent (vol) water. Isobutanol of 99 percent purity containing 0.06 percent (vol) water and the butanol isomers as impurities was chosen as a representative cosolvent. The function of the cosolvent is to prevent phase separation which isobutanol does at 25°C and less than 0.08 percent (vol) water in a methanol-gasoline blend. Demineralized tap water was used to adjust the blends to the desired 0.05 percent (vol), the concentration chosen as representative of commercial fuels handled with reasonable housekeeping procedures.

Test solutions were blended for each additive and controls in 8 liter volumes, the minimum necessary to provide adequate amounts for the individual tests, water determinations and any replacements that might be needed for accidental losses. This ensured that there would be little chance of anomalies in the test results arising from inconsistencies in

TABLE II. PROPERTIES OF GASOLINE BLENDING COMPONENTS

Gravity, °API	60.4
Hydrocarbons, Vol %	
Saturates	66.8
Olefins	9.0
Aromatics	24.2
Water, Wt %	0.006
Sulfur, Wt %	0.02
D86 Distillation	
% Evaporated/°C	
IBP	32
10	50
50	103
90	174
EP	215

mixing procedures. Prior to mixing a test solution, the additive solution was mixed well with the required amount of gasoline and a well-mixed solution of the alcohols and water was made. The volume of water needed to bring the solution up to 0.05 percent (vol) was calculated from the amount of water contained in the blending components as determined by Karl-Fischer titrations. Random determinations of water in 10 of the test solutions gave an average water content of 0.048±0.004 percent by volume.

The alcohol mixture was added slowly with constant agitation to the gasoline to ensure complete mixing and keep the water from separating. The volumes of the individual blending components used in preparing the individual test solutions are shown in Table III.

TABLE III. BLENDING COMPONENT VOLUMES USED TO PREPARE LABORATORY TEST SOLUTIONS

Methanol Volume %	Gasoline Volume, mL	Additive Solution Volume, mL	Methanol Volume, mL	2-Butanol Volume, mL	Water Volume, mL
0	8000	0	0	0	0
2.5	3760	4000	200	40	4
5.0	3520	4000	400	80	4
10.0	3040	4000	800	160	4
20.0	2080	4000	1600	320	4

A problem arose in blending the test solution containing additive D which would separate when mixed by this procedure. It was found that a homogeneous solution would result if the additive was dissolved in the alcohol mixture which was then added to the gasoline with constant and vigorous stirring. All subsequent solutions containing additive D were made in this manner.

The test solutions for Phase I were blended to contain the additives in the concentrations shown in Table I. The three additives used in Phase II were blended singly and in binary combinations in blends containing 5, 7.5 and 10 percent methanol. The procedure described above was used to make the Phase II test solutions containing the additive concentrations shown in Table IV.

TABLE IV. ADDITIVES USED IN PHASE II TEST SOLUTIONS

Test Code	Additive	Concentration, lb/TBL
D	D	2 x vol % methanol
3B	B	9
BD	B+D	3 + 2 x vol % methanol
3BD	B+D	9 + 2 x vol % methanol
BE	B+E	3 + 15
DE	D+E	2 x vol % methanol + 15

The solution codes indicate the amount of additive used as a multiple of the Phase I concentration; for example, 3BD means the test solution contained three times the concentration of B and the same of D as used previously. The concentration of additive D in these solutions varied as a function of the methanol percentage in the final blend. Hence, the solutions contained 10, 15 or 20 lb/TBL additive D in 5, 7.5 or 10 percent (vol) methanol, respectively, while the concentration of the second additive was the same regardless of methanol content. These solutions were mixed carefully with constant stirring to ensure that the increased concentrations of additives did not cause phase separation.

Metals representative of those used in automotive fuel systems were used in the solution corrosivity tests. The ten metals specified for these determinations (aluminum, zinc, carbon steel, stainless steel, terneplate, cast iron, brass, bronze, magnesium and copper) were obtained in 1-mm thick specimens, 50-mm long by 13-mm wide. There are no standard methods available for this type of corrosion testing but there do exist recommendations from various sources(4-10) which are applicable in some respects. Applicable sections of these articles were used to formulate the corrosion test procedures reported here.

The metal specimens were prepared for testing by first washing with acetone and then polishing with 600 grit silicon carbide abrasive. The polished specimens were rinsed with acetone and dried. Any specimens having visible imperfections were rejected from further use. The test cells consisted of a 500-mL French square screw cap bottle equipped with a Polyseal cap liner. The specimen was suspended by a piece of twine affixed to the cap liner. Each bottle was charged with 250-mL test solution and the twine length was adjusted to allow suspension of half the metal specimen in the solution. This arrangement gave a fluid volume to specimen surface area ratio of 0.35 mL/mm^2 and allowed half of the specimen to be exposed only to the solution vapors. Each bottle contained only one metal specimen to avoid any dissimilar metal ion effects.

The bottles containing the test specimens half immersed in the test solution were placed in deep aluminum trays for ease of handling and to contain any breakage. These trays containing the test cells were placed in a constant temperature chamber maintained at 43°C. The 30-day test period was interrupted at the 15-day mark to reaerate with filtered compressed air. This was done in order to replenish consumed oxygen in the test bottle.

For corrosivity determinations in Phase II, the number of test metals used in Phase I was reduced to six - copper, brass, bronze, terneplate, magnesium and zinc. The solution corrosivity tests in Phase II were conducted identically to the previous procedure with all previously unused materials. The Phase I tests with aluminum, zinc, carbon steel, stainless steel and cast iron were continued through Phase II with reaeration of the solutions done at the same time as the Phase I test solutions.

Materials for compatibility testing were chosen from the two major classes of synthetic elastomers and plastics, in addition to a naturally occurring compound. These materials represent as broad a range of applications and chemical types as could reasonably be tested within the scope of the program. The twelve materials used in the compatibility tests are:

1. Epichlorohydrin elastomer, a chloropropylene epoxide polymer,

2. Fluorocarbon elastomer, a vinylidene fluoride and hexafluoropropylene copolymer,

3. Nitrile (NBR) - high acrylonitrile elastomer, a butadiene-acrylonitrile copolymer,

4. Nitrile (NBR) - low acrylonitrile elastomer, a butadiene-acrylonitrile copolymer,

5. Fluorosilicone elastomer, a fluorinated silicon oxide polymer,

6. Neoprene elastomer, a chloroprene (chlorobutadiene) polymer,

7. Acetal resin, a copolymer of a formal and glycol,

8. Polyethylene-high density, an ethylene polymer,

9. Polypropylene-high density, a propylene polymer,

10. Nylon, a polyamide made from dicarboxylic acids and diamines

11. Perfluorocarbon, a fully fluorinated linear polymer, and

12. Cork gasket material made from cork oak.

The materials selected for testing in this project were used by ARCO Chemical Company(3) to acquire the data they submitted in support of their waiver request to the U.S. Environmental Protection Agency for the use of Oxinol, a mixture of methanol and tertiary butanol, as a blending component for unleaded automotive gasoline. The nonmetals used for testing are considered to be representative of the materials used in automotive applications, to provide a reasonably broad range of chemical and physical properties and to be exposed to automotive fuels under various conditions. The choice of these materials was made by NASA and DOE personnel based primarily on these considerations.

Standard test methods for the determination of physical properties of rubber and plastics(11-14) were used to determine effects of the methanol-gasoline blends on the nonmetals. The properties of tensile strength and ultimate elongation were measured with commercial instruments available in our laboratories. Hardness was determined for the elastomers with a Shore A tester and for the plastics with a Shore D tester. These properties were determined on test specimens before and after immersion in control and test solutions. The effects of methanol on the materials could then be detected and any changes in these effects caused by the test additives would be noted.

The materials were obtained as 3-mm thick sheets except the cork gasket material was 6-mm thick. The elastomers and plastics were cut into test coupons with a size C dumbbell shaped die and the cork was cut with a razor blade into 50-mm by 25-mm rectangles. The dumbbell shaped specimens were cut by placing the knife edge of the die on the sample sheet located on the anvil of a hydraulic press. The press was then actuated and the piston drove the die cleanly and quickly through the sheet. The resultant specimens were free of ragged edges and burrs. The acetal resin and nylon were too brittle to cut with the die and were obtained in thinner sheets of 1.5-2-mm thickness. These were cut with the size C die without any cracking.

Replicate determinations of tensile strength, ultimate elongation, volume swell and hardness were made on all of the elastomers and plastics. Only thickness could be effectively measured on the cork; this was done at three points with a micrometer on the ends and the middle of the specimen and averaged. The specimens were then placed in a test tube to soak in test solution for a period of 72 hours at ambient temperature, 23°C. Three test specimens of one material were suspended in each solution by means of a wire affixed to a cork stopper.

At the end of the test period the specimens were removed and any fuel not drained off was removed by briefly dipping in acetone. The specimens were dried by blotting with a paper towel. The property determinations made prior to soaking were repeated immediately after soaking for comparison to determine the effects of soaking in the test solutions. At th- end of the Phase I test period, these observations were compared to the SAE allowable pass criteria(15) shown in Table V.

TABLE V. SAE PERFORMANCE CRITERIA FOR NONMETALS

ASTM Method	Determination	Pass Criterion
	Elastomers	
D 412	Tensile strength	Lose 50% maximum
D 412	Ultimate elongation	Lose 50% maximum
D 471	Volume swell	0-25%
D 2240	Shore A hardness	Lose 20 points maximum
	Plastics	
D 638	Tensile strength	Lose 30% maximum
D 638	Elongation	--
D 471	Volume swell	0-25%
D 2240	Shore D hardness	Lose 20 points maximum
	Cork	
D 471	Change in thickness	25% maximum

The Phase II testing of materials was conducted in the same manner except that the number of substances was reduced to six. These six materials consisted of three elastomers, two plastics and the cork gasket material. A reduction in the number of nonmetals to be evaluated in Phase II was necessitated by the constraints of time and funding. The six materials chosen (fluorocarbon, nitrile high acrylonitrile, neoprene, nylon, perfluorocarbon and cork) were selected on the basis of more extensive use in automotive fuel systems.

RESULTS AND DISCUSSION

Metals

Control determinations consisted of the corresponding material specimens exposed to gasoline containing the alcohols at appropriate concentrations but no additives. Results of exposure of metal test specimens immersed in alcohol-gasoline blends containing the test additives were compared with control exposures. All comparisons were made within a material group only. In no case were observations or ratings made on one material compared with those made on another; the results allowed only qualitative intercomparisons to be made. Rigorous quantitative intercomparisons would require that the origin of the different color responses for each metal be known.

Within the first week of the test, six of the magnesium specimens immersed in the 20 percent methanol solutions had completely disintegrated after falling into the test solution. Only the specimen in the blend containing additive D remained intact during the first two weeks of the test. Severe corrosion had occurred at the hole where the twine was tied and the metal specimen broke off at this point when the container was moved for reaeration. In all of these tests corrosion, which started at the hole used to suspend the specimen, was visible within 72 hours of the beginning of the test. The specimens eventually fell into the solutions where the reaction continued until disintegration was complete and only a layer of powder-like material was visible at the bottom of each bottle. The test in 20 percent methanol-gasoline was discontinued at this time but the remainder of the magnesium specimens immersed in test solutions remained intact for the duration of the test. Brass, bronze, copper and terneplate exhibited visible effects--for the most part color changes--at the end of the 30-day test period. None of the metals in the neat gasoline control solutions exhibited any detectable changes.

Aluminum, zinc, carbon steel, stainless steel, and cast iron showed no corrosivity effects at the end of the 30-day test period of Phase I. In order to enhance the chances of detecting any effects these tests were continued to the end of Phase II. Reaeration of these test solutions was done at the midpoint of the Phase II test period. When the five tests were terminated at the end of Phase II the metals were inspected for corrosivity effects. There were neither any weight changes nor visible effects noted on any of the specimens.

Except for occasional, randomly occurring pits noted especially in the bronze specimens there was little evidence that pitting would be of much use in assessing the extent of corrosion. There was no measurable weight change on any of the randomly selected metal test specimens. Even the magnesium coupons which had been immersed in the 10 percent methanol blends neither lost nor gained any weight.

With the exception of bronze, changes in coloration were left as the major apparent effect of corrosive action of the methanol-gasoline blends. Assuming that these effects were corrosion related and keeping in mind that some additives provide corrosion protection by forming a film on the metal surface, the test strips were ranked by visual inspection relative to the control within each methanol-concentration group. The test strips were ranked according to the severity of corrosive effects within a group defined by the type of metal exposed and the methanol concentration of the test solution. These rankings were called "less" or "more" with respect to the corrosion severity of a control solution containing no additive. The rankings resulting from these visual evaluations are shown in Table VI.

The metal specimen taken from a control fuel blend, designated Ⓚ in the table, was compared to each specimen belonging to that concentration group. Each specimen taken from an additive-containing solution in that group was rated as to whether it exhibited more or less corrosion than the control. Once these designations were made, the test specimens were compared to each other and the final rankings were made. The assessment of corrosion severity was made more difficult by the different colors of the test specimens attributable to the different additives. The rankings shown in Table VI must be qualified by these factors. The most that can be said about the relative positions of the specimens within a concentration group is that corrosion severity of any one is equivalent to or less than its nearest neighbor on the right and transposition of two adjacent results is not allowed. In some cases corrosion severity of a test specimen was obviously very much less than that of its corresponding control and this is illustrated in Table VI by the additive codes in italics.

Assuming that these observations were actually being made of solution corrosivity effects, the additives to be tested in Phase II were chosen. Based on these subjective evaluations and consultation with the NASA project manager, it was decided that only additives B and D seemed to have any significant inhibitory effects on corrosion of the brass and bronze specimens. Additive E apparently had a similar inhibitory effect of the fuel's corrosiveness toward terneplate. Additive F also seemed to

TABLE VI. RANKING OF METAL TEST SPECIMENS ACCORDING TO CORROSION SEVERITY — PHASE I

Methanol Content, vol %	Corrosion Severity* Low						High
			Brass				
2.5	C	Ⓚ	E	A	B	D	F
5	Ⓚ	C	B	D	A	F	E
10	*D*	*B*	Ⓚ	C	E	A	F
20	*A*	*B*	*D*	Ⓚ	F	E	C
			Bronze				
2.5	Ⓚ	E	C	F	A	B	D
5	D	Ⓚ	B	C	A	F	E
10	B	D	Ⓚ	F	C	E	A
20	*A*	C	Ⓚ	F	B	D	E
			Copper				
2.5	Ⓚ	D	C	E	F	A	B
5	Ⓚ	B	E	D	F	A	C
10	E	Ⓚ	D	B	A	F	C
20	Ⓚ	B	C	A	F	E	D
			Terneplate				
2.5	*E*	*F*	*C*	D	Ⓚ	B	A
5	F	Ⓚ	E	D	C	A	B
10	*F*	*E*	D	C	A	Ⓚ	B
20	B	Ⓚ	F	E	C	A	D
			Magnesium				
2.5	Ⓚ	C	B	D	A	F	E
5	Ⓚ	D	C	B	A	E	F
10	Ⓚ	A	B	E	D	C	F
20	D	All others failed					

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*Ⓚ = control value; italics indicates significantly less corrosion severity relative to control.

impart some corrosion inhibition in the terneplate system but was eliminated because of its very high formulating cost.

The three additives B, D and E, were tested in Phase II under the same conditions of time and temperature but the concentration of methanol and formulation of the additives were changed. Decreasing the methanol concentration levels to three and the metals to six (brass, bronze, copper, terneplate, magnesium and zinc), reduced the number of tests to almost half that of Phase I. Potentially, more useful information could be realized from Phase II as a result of formulating the test solutions to contain the three additives both singly and in combination and at increased concentrations. The test with additive D was repeated at the same concentration used in Phase I as a confirmatory measure and to serve as a control between the two phases. Since additive B had been formulated at the lowest concentration of the six additives used in Phase I it was an attractive choice - from an economics standpoint - for further testing. If it were effective as a corrosion inhibitor, an increase in concentration should help to confirm this effect by enhancing the protection thereby making it more readily detected. The formulation of the additives as binary mixtures was expected to help determine if there would be any synergistic effects resulting from combining the components.

The additives were evaluated as metal corrosion inhibitors by ranking the results of the Phase II tests as shown in Table VII and comparing to the Phase I corrosivity results. The Phase II results were ranked differently than previously in that the evaluator had only a code number for identification of the test solutions, hence there was no prior knowledge of additive content and component concentrations to bias the results. Corrosion severity was rated on a subjective scale of light, medium, and heavy which was further classified as to degree of corrosion on a numerical scale as shown in the table.

These evaluations, with one exception, were based on visible effects noted on the part of the metal specimen immersed in test solution. There was no detectable effect on the immersed part of the magnesium in either Phase I or II; all of the effects were noted on the part of the metal specimen exposed to solution vapors. The other metals were either not affected by the vapor phase or where there was some effect it was not clear whether it was from the vapor, from solution creep, or from a combination of the two. Because of this, vapor phase effects were disregarded except for magnesium.

TABLE VII. RANKING OF METAL TEST SPECIMENS ACCORDING TO CORROSION SEVERITY — PHASE II

Methanol Volume %	CORROSION SEVERITY*									
	Light			Medium				Heavy		
	1	2	3	4	5	6	7	8	9	10
BRASS										
5 0		BD,3BD				Ⓚ,3B	D		BE,DE	
7 5		3BD				Ⓚ	BE		DE	3B,BD,D
10 0		3B,D,BD			3BD	Ⓚ		BE	DE	
BRONZE										
5 0		D				3B,BE,BD,DE,3BD		Ⓚ		
7 5						Ⓚ,3B,BD,3BD		D,BE,DE		
10 0						Ⓚ,3B,BD,BE,DE,3BD		D		
COPPER										
5 0			DE			Ⓚ,3BD		3B	BE	D,BD
7 5			BD,DE,3BD			Ⓚ,3B	BE			D
10 0						Ⓚ,3B,BD,DE,3BD	D,BE			
TERNEPLATE										
5 0						Ⓚ,3B,3BD,BE,DE	D,BD			
7 5	3BD			3B	D,DE		Ⓚ,BD,BE			
10 0	BE			BD	D		Ⓚ,3B,3BD,DE			
MAGNESIUM										
5 0	Ⓚ		3BD			BD		D,DE	3B	BE
7 5	Ⓚ		BD,3BD			3B	D	DE		BE
10 0	Ⓚ		D,DE			BD,3BD	3B	BE		

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* Ⓚ = control value

The main consideration in evaluating these results is that the corrosivity test was a short-term study and the noted effects were not fully characterized nor correlated with field applications. Ordinarily, the assessment of corrosivity in laboratory tests is based on weight change and pitting of the test specimens but neither of these conditions occurred in this test series with the exception of bronze, which pitted lightly. Hence, with the exception of bronze, only the changes of color detected on the metals at the end of the test periods were used to determine corrosion severity. Because of the lack of available information on the long-term effects of methanol-gasoline fuels, especially in field use, it was assumed that the observed effects were, in fact, manifestations of the corrosivity of these fuels.

Since it was the purpose of this project to screen currently available, commercial additives for possible use in methanol-gasoline fuels, the conclusions drawn from the observed results should be considered guides to the use of these additives. The use of any of these additives for a specific application warrants confirmation of its efficacy by further experimentation under appropriate conditions.

Generally, the Phase I corrosivity test results indicated that additives B and D might provide some protection to brass and bronze materials and additive E to terneplate components. These three additives were tested in Phase II in higher concentration than in Phase I and in combinations of two additives to determine if there would be any enhancement of protection. Additive D was used as a control by retesting in the same concentration as Phase I. If only the response of the metals immersed in blends containing D relative to that in the methanol-gasoline controls is considered, the test repeats quite well in Phase II. This indicates the test is reliable to the extent that the subjective repeatability determinations are reliable.

If the corrosivity results of the Phase II tests with three additives are considered separately, those for additive B repeat from Phase I to Phase II for copper and terneplate. As stated above, the tests with D repeat well for all five metals. The test results with additive E also repeat well and can be used to confirm the repeatability of the corrosion testing procedures. The corrosion protection being sought was apparently provided by additive B for brass, copper and terneplate as shown in Table VII. Additive D apparently provided corrosion protection for brass and copper. The combination of these two additives seemed to provide enhanced protection in varying degrees for four metals, brass, bronze, copper and terneplate. Additive E did not provide corrosion protection and combining it with the other additives had no detectable effect except for the combination with D which seemed to improve somewhat the protection for copper. Because these evaluations are based on short-term testing results, further work would be required to determine the full extent of protection that could be provided by any of these additives. Additive E apparently contributes to increased corrosivity of the methanol-gasoline fuels but this cannot be determined from these data, and confirmation of this observation would require further experimentation. As in Phase I, there were no detectable effects on zinc in any of the test solutions of Phase II.

Nonmetals

The materials compatibility studies were guided by information from the additive suppliers concerning the effects of the additives on polymeric materials. All indications were that there are no known additives that will lessen the effects of methanol on these materials. Alcohols will generally aggravate incompatibilities between gasoline fuels and polymeric fuel system materials, and these tests were conducted to ascertain that the candidate additives would not cause any additional compatibility problems.

The properties measured to determine compatibilities were tensile strength, ultimate elongation, volume swell and hardness for the elastomers. Dimensional (thickness) change was substituted for volume swell determinations in the case of the cork and was the only determination that could be made on the gasket material. The evaluation of the results of these determinations proved to be a formidable task since there were over 1000 data points for each phase. Preliminary inspection of the data from Phase I indicated the information obtained from the additive suppliers was essentially correct as the additives seemed to have no detectable effects on the values of these properties.

In the interest of brevity and in an attempt to make the data more manageable, the results of these determinations were averaged for the six additive-containing fuels in each methanol concentration group for comparison to the corresponding control. The standard deviation, σ n-1, was calculated for each average value. The results of the material compatibility tests calculated in this way are shown in Tables VIII and IX. The control values listed as Ⓚ are the property measurements made on the test coupons which had been immersed in gasoline or methanol-gasoline blends not containing the test additives. The nonmetals used for the Phase II tests consisted of three elastomers, two plastics, and cork gasket material as listed in Table IX and described in the Experimental Program section.

TABLE VIII. POLYMERIC MATERIAL COMPATIBILITY PROPERTIES IN METHANOL–GASOLINE SOLUTIONS — PHASE I

Methanol Volume %	Tensile Strength % Retained		Ultimate Elongation % Retained		Volume Swell % Increase		Hardness Points Decrease	
	[a]Ⓚ	[b]$\bar{A} \pm \sigma_{n-1}$	Ⓚ	$\bar{A} \pm \sigma_{n-1}$	Ⓚ	$\bar{A} \pm \sigma_{n-1}$	Ⓚ	$\bar{A} \pm \sigma_{n-1}$
	Epichlorohydrin							
0	53.2		62.8		17.8		6	
2.5	46.0	40.8±5.5	52.0	46.3±7.4	34.6	37.6±1.3	9	10.3±0.9
5.0	33.3	33.8±3.7	42.2	39.9±4.4	48.0	50.3±3.5	12	12.0±1.0
10.0	26.9	31.8±3.0	37.9	39.5±3.8	49.0	60.3±1.2	12	12.5±0.5
20.0	36.2	36.2±2.0	45.9	41.4±4.2	54.0	55.8±2.2	11	11.5±1.0
	Fluorocarbon							
0	86.1		82.4		5.3		4	
2.5	84.5	90.5±1.4	86.9	87.7±1.9	8.3	7.4±0.6	10	6.7±1.[illegible]
5.0	80.9	82.0±4.0	89.6	81.1±2.2	10.5	11.2±0.6	7	10.7±2.4
10.0	70.6	73.6±4.1	74.7	75.8±0.7	16.1	15.5±0.5	9	11.3±1.1
20.0	67.5	64.7±1.2	77.4	73.4±2.1	19.1	19.2±0.6	12	13.2±1.8
	Nitrile-H							
0	73.0		74.7		22.6		8	
2.5	62.8	68.5±8.2	69.8	69.1±3.7	27.3	26.8±6.7	10	9.8±0.7
5.0	59.0	61.8±2.7	67.5	66.1±4.2	34.8	31.7±7.5	11	10.2±1.1
10.0	62.5	60.4±1.8	66.0	63.0±3.0	38.8	36.5±5.9	11	10.5±0.8
20.0	60.1	62.4±3.2	65.4	65.6±5.9	39.8	36.8±6.0	13	11.3±1.8
	Nitrile-L							
0	62.9		82.9		30.8		8	
2.5	54.3	50.8±2.6	72.2	67.7±3.9	41.9	41.9±0.9	13	14.1±1.0
5.0	48.2	41.3±4.2	64.5	69.3±4.4	46.5	48.0±4.0	11	13.8±1.1
10.0	48.2	48.3±3.3	59.2	65.5±6.0	51.1	52.4±1.8	10	13.3±1.2
20.0	48.0	49.6±3.9	66.8	66.0±5.8	53.8	44.9±9.4	12	13.5±1.4
	Fluorosilicone							
0	52.0		62.4		22.2		15	
2.5	35.3	28.7±5.3	65.2	50.1±4.0	37.4	38.3±0.4	17	16.3±1.2
5.0	29.0	27.4±3.6	60.2	58.4±2.7	38.3	39.8±0.5	16	17.0±2.0
10.0	28.4	27.8±4.4	60.9	58.6±1.6	38.7	39.9±0.6	16	16.5±1.2
20.0	27.4	27.7±3.3	58.7	58.5±1.7	38.7	38.7±0.7	17	16.2±0.4
	Neoprene							
0	55.2		66.2		42.0		12	
2.5	55.4	57.0±5.8	68.5	68.7±4.5	46.3	44.1±1.1	15	12.3±0.7
5.0	56.6	56.8±3.4	66.7	69.9±3.6	41.5	41.6±1.5	14	13.5±1.2
10.0	56.1	57.2±3.4	67.7	70.4±4.2	38.8	38.4±1.3	14	13.7±0.5
20.0	61.0	58.8±6.3	68.5	70.5±5.9	34.7	33.5±0.5	13	13.0±2.2
	Acetal							
0	96.0		100.0		1.6		2	
2.5	95.6	95.6±0.4	100.2	100.0±1.4	1.6	1.7±0.2	0	1.5±1.2
5.0	94.9	95.0±0.3	99.2	98.3±1.2	1.5	1.6±0.1	2	1.0±0.8
10.0	95.0	94.9±0.2	99.9	99.2±1.5	1.5	1.6±0.1	1	0.5±0.8
20.0	94.3	94.9±0.2	97.4	97.8±1.2	1.7	1.7±0.2	1	1.0±0.8

TABLE VIII. POLYMERIC MATERIAL COMPATIBILITY PROPERTIES IN METHANOL-GASOLINE SOLUTIONS — PHASE I (Cont'd)

Methanol Volume %	Tensile Strength % Retained		Ultimate Elongation % Retained		Volume Swell % Increase		Hardness Points Decrease	
	[a]Ⓚ	[b]$\bar{A} \pm \sigma_{n+1}$	Ⓚ	$\bar{A} \pm \sigma_{n+1}$	Ⓚ	$\bar{A} \pm \sigma_{n+1}$	Ⓚ	$\bar{A} \pm \sigma_{n+1}$
	Polyethylene-High Density							
0	97.2		98.1		2.4		2	
2.5	94.5	94.1±0.3	102.3	100.7±1.0	3.0	2.1±0.1	0	1.5 1.2
5.0	93.7	93.9±0.2	103.1	100.8±1.5	2.4	2.1±0.1	2	1.0 0.8
10.0	94.0	94.0±0.4	101.5	100.5±1.6	2.6	2.0±0.1	1	0.5 0.8
20.0	92.3	94.2±0.5	100.2	99.5±1.9	2.4	2.1±0.1	1	1.0 0.8
	Polypropylene-High Density							
0	93.2		94.8		4.7		[c]-2	
2.5	95.3	95.1±0.2	96.0	95.0±1.4	4.1	1.4±0.1	-3	-1.2 0.7
5.0	94.7	95.0±0.1	95.6	95.7±1.6	3.6	1.3±0.2	-1	-0.8 0.7
10.0	95.4	95.2±0.4	95.1	95.5±1.0	3.4	1.2±0.0	-1	-0.7 0.7
20.0	95.0	94.6±0.5	96.3	95.7±1.2	3.4	1.2±0.2	-1	-0.8 0.7
	Nylon 6/6							
0	97.0		100.9		0.1		-5	
2.5	94.0	94.6±0.4	112.8	110.7±1.0	1.4	1.3±0.1	-5	0.5 1.5
5.0	93.4	93.3±0.7	116.7	115.0±1.4	1.3	1.3±0.1	-5	-0.8 1.0
10.0	93.0	93.1±0.5	112.3	110.3±1.9	1.2	1.3±0.0	-3	-1.0 0.8
20.0	91 2	91.9±0.5	115.3	112.2±1.7	0.8	1.2±0.1	-3	-1.5 0.5
	Perfluorocarbon							
0	80.4		81.3		1.4		3	
2.5	81.2	81.4±1.2	83.6	83.9±0.2	1.3	1.2±0.1	3	1.0 0.8
5.0	82.4	81.4±1.2	84.8	83.8±0.4	1.0	1.2±0.1	1	0.5 0.8
10.0	84 7	83.7±0 4	82.7	82.5±0.3	1.2	1.2±0.1	4	2.7 0.5
20.0	81 7	81.9±0.6	82.7	83.2±0.3	1.3	1.2±0.1	3	2.5 0.8
	Cork							
0	-	-	-	-	[d]0.7		-	-
2.5	-	-	-	-	0.6	0.6±0.1	-	-
5.0	-	-	-	-	0.7	0.7±0.1	-	-
10.0	-	-	-	-	0.7	0.7±0.1	-	-
20.0	-	-	-	-	0.8	0.7±0.1	-	-

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[a] Ⓚ = Control value

[b] $\bar{A} \pm \sigma_{n+1}$ = average value and standard deviation for additive-containing blends

[c] Negative value indicates increase in hardness

[d] Dimensional (thickness) change

TABLE IX. POLYMERIC MATERIAL COMPATIBILITY PROPERTIES IN METHANOL-GASOLINE SOLUTIONS — PHASE II

Methanol Volume %	Tensile Strength % Retained		Ultimate Elongation % Retained		Volume Swell % Increase		Hardness Points Decrease	
	[a]Ⓚ	[b]$\bar{A} \pm \sigma_{n-1}$	Ⓚ	$\bar{A} \pm \sigma_{n-1}$	Ⓚ	$\bar{A} \pm \sigma_{n-1}$	Ⓚ	$\bar{A} \pm \sigma_{n-1}$
	Fluorocarbon							
0	76.2		78.3		9.1		5	
5.0	66.0	61.4±2.3	77.4	81.7±3.8	16.7	14.5±2.3	9	10.2±1.2
7.5	65.7	67.4±6.4	75.1	77.2±2.9	15.9	18.3±4.5	11	10.8±0.8
10.0	61.9	74.1±5.8	76.3	76.3±1.2	18.9	18.9±1.9	9	10.3±1.2
	Nitrile-H							
0	97.7		82.2		15.4		6	
5.0	65.3	61.4±2.1	76.8	72.2±2.8	32.9	32.2±1.0	11	10.3±0.8
7.5	62.1	62.1±1.9	74.9	70.5±1.2	36.3	35.1±0.8	12	11.5±1.2
10.0	58.3	62.7±1.9	70.0	69.3±3.2	35.0	37.0±1.0	12	11.8±2.0
	Neoprene							
0	48.8		66.5		41.3		11	
5.0	56.0	57.1±1.6	69.3	71.7±2.0	40.1	41.0±1.6	12	12.7±0.5
7.5	50.8	54.8±1.2	71.4	72.5±1.8	37.5	39.7±0.9	13	12.4±0.5
10.0	55.2	55.8±4.4	72.6	72.2±3.1	35.0	37.0±0.6	13	12.5±0.5
	Nylon 6/6							
0	97.2		102.8		0.5		2	
5.0	93.4	93.9±0.6	117.1	109.7±5.1	1.1	0.9±0.2	0	1.6±0.9
7.5	94.7	93.4±1.0	120.0	108.3±3.8	1.0	0.9±0.1	0	1.2±0.9
10.0	93.1	94.1±0.8	113.4	110.3±4.0	0.9	0.9±0.1	1	1.2±0.9
	Perfluorocarbon							
0	100.6		91.7		0.1		0	1.3±1.0
5.0	112.0	100.4±2.3	84.6	87.7±4.3	0.2	0.37±0.39	1	0.8±0.7
7.5	105.3	102.4±6.8	82.5	84.6±2.7	0.2	0.15±0.05	1	1.5±1.0
10.0	106.1	107.1±5.7	82.5	84.3±3.1	0.2	0.25±0.13	4	-
	Cork							
0	-	-	-	-	[c]1.2	-	-	-
5.0	-	-	-	-	6.3	7.4±0.6	-	-
7.5	-	-	-	-	6.9	6.7±0.4	-	-
10.0	-	-	-	-	6.3	6.9±1.0	-	-

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[a]Ⓚ = Control Value

[b]$\bar{A} \pm \sigma_{n-1}$ = average value and standard deviation for additive-containing blends

[c] = Dimensional (thickness) change

The main conclusion drawn from the results of these determinations is that, as expected, the additives have no effect on the tensile properties of the nonmetals. The measured values of these properties of the nonmetals after immersion in fuel blends containing additives did not differ significantly from the control values. The correspondence of values is much closer between controls and the respective additive tests than it is between the controls in the two Phases. As an example, the value for tensile strength of neoprene after immersion in neat unleaded gasoline changes about 12 percent from 55.2 in Phase I to 48.8 in Phase II. The difference between the control (55.4 for 2.5 percent methanol, Table VIII) and the additives average response (57.0 for 2.5 percent methanol, Table VIII) is, in most cases less than 5.0 percent. For the most part this relationship holds true between the values of the tensile properties of all the materials after immersion in the control and test solutions. This indicates that any response differences noted rise from method variability rather than additive effects. A more rigorous statistical analysis is required to test this hypothesis but was outside the scope of this program.

Bar graphs of the Phase I property data of the elastomers immersed in methanol-gasoline control solutions are shown in Figures 1 to 4. Since these fluids did not contain the test additives, the results show the concentration dependent effects of methanol on elastomer integrity. The effects of the solutions containing test additives were no different from those shown in the figures indicating the additives did not modify the effects of the methanol.

Figure 1 is a plot of Phase I tensile strength data for the elastomers. Applying the pass criterion (Table IV) of 50 percent retention, the epichlorohydrin and fluorosilicone failed at all concentrations of methanol, and nitrile-low acrylonitrile was marginal. As seen in Figure 2, epichlorohydrin also failed the requirement of 50 percent retained elongation at methanol concentrations of 5 volume percent and above. Figure 3 shows that with methanol present only the fluorocarbon elastomer consistently passed the volume swell criterion of 25 percent maximum increase. Figure 4 indicates the generally deleterious effect of methanol on elastomer hardness, but all results were within the requirement of a hardness loss of no more than 20 points.

Since property changes for the plastics and cork were slight, no bar charts are presented for these materials. The most notable feature of these data was the high loss in tensile strength and retained elongation for the perfluorocarbon relative to the other plastics.

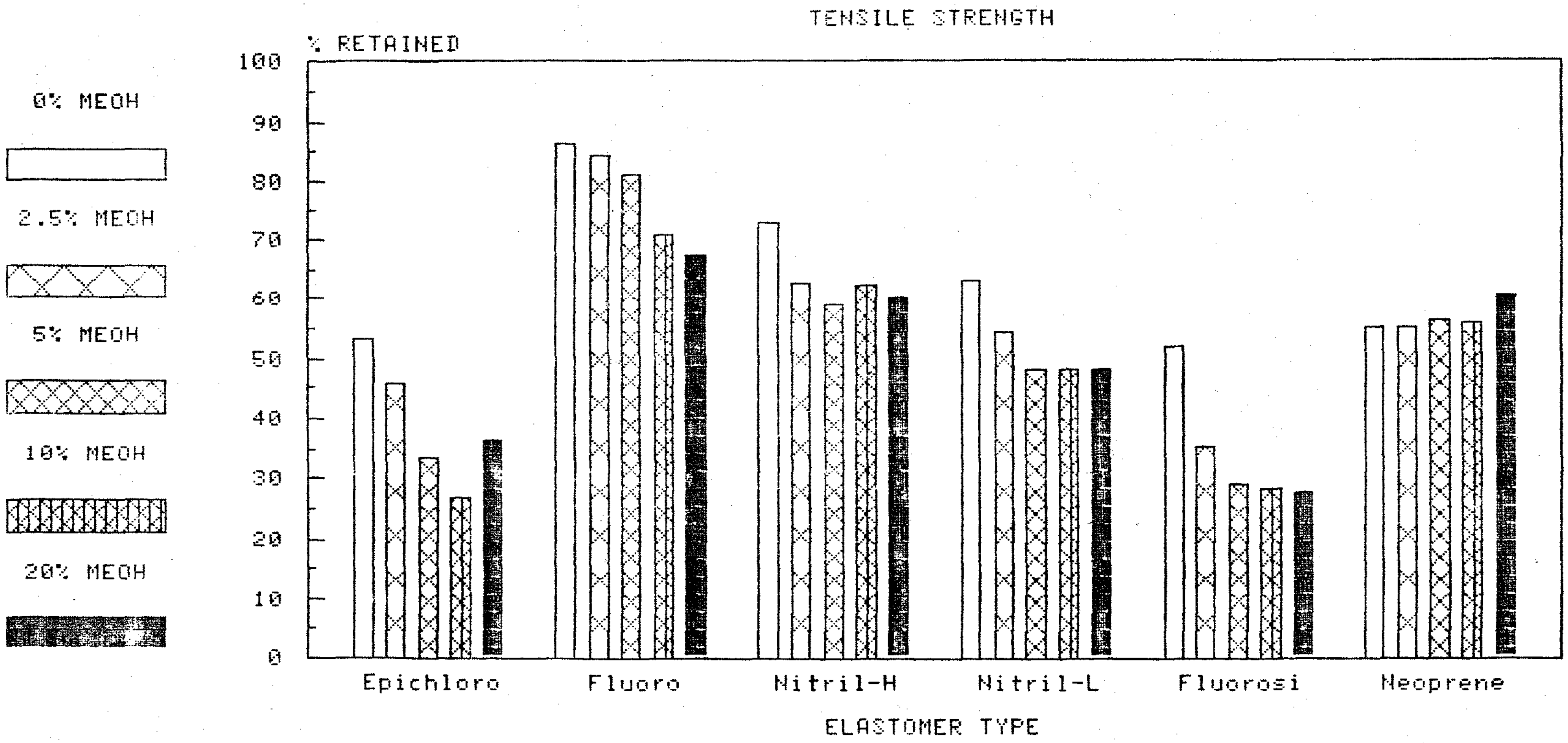

FIGURE 1. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER TENSILE STRENGTH -- PHASE I

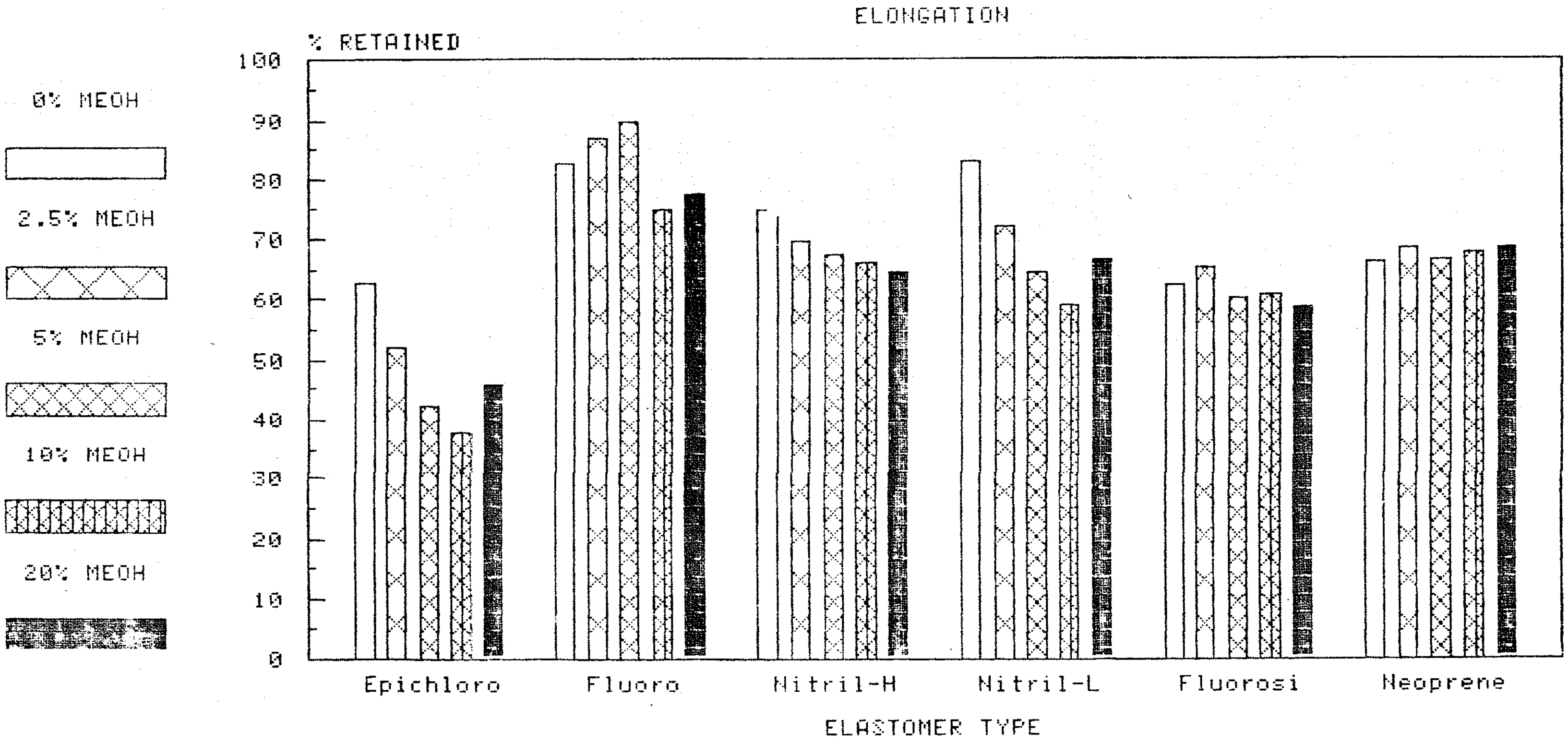

FIGURE 2. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER ELONGATION -- PHASE I

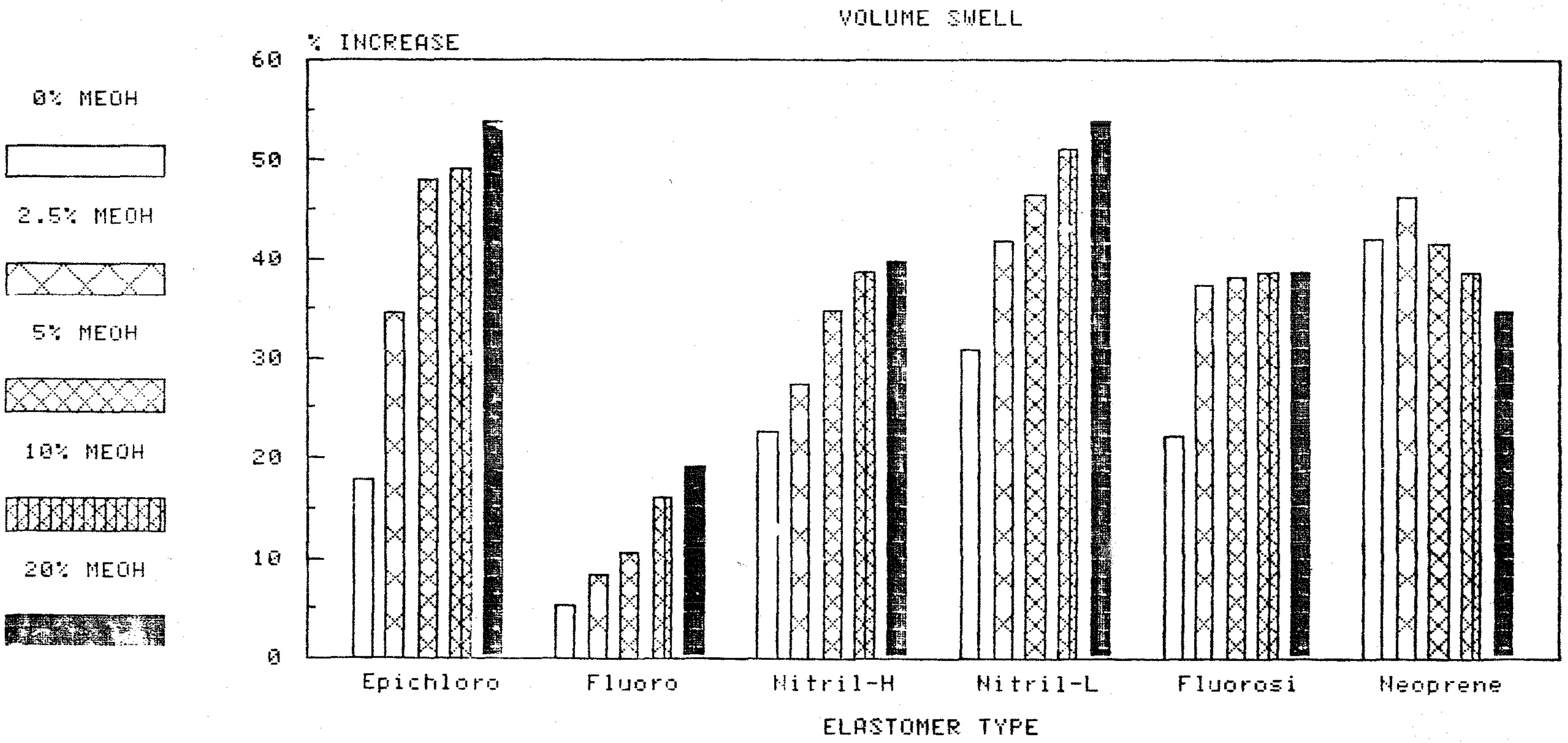

FIGURE 3. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER VOLUME SWELL — PHASE I

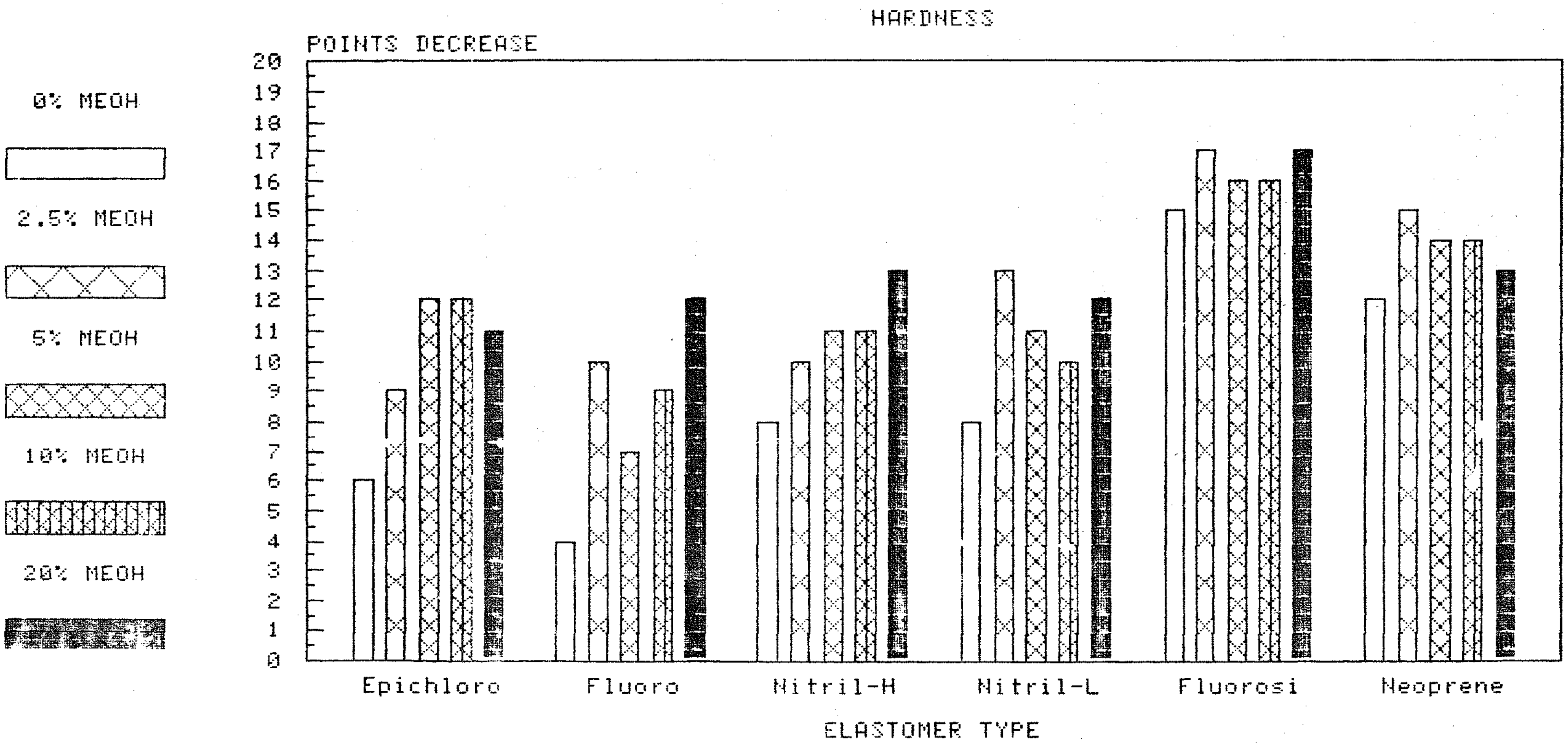

FIGURE 4. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER HARDNESS — PHASE I

The results of all material compatibility testing for Phase II are listed in Table IX, and the elastomer data for the control solutions are plotted in Figures 5-8. The latter data, within experimental variance, are in agreement with observations made in Phase I. The other nonmetal property results are in similar agreement except that the degree of tensile strength loss noted in Phase I for the perfluorocarbon was not confirmed in Phase II. In general, no deleterious effects were observed in Phase II as a consequence of additive treatment of the gasoline-methanol blends.

The material compatiblity tests confirmed that methanol in gasoline has deleterious effects on polymeric materials. Additives in these methanol-gasoline blends did not modify the observed effects in any discernible manner. Hence, these additives, subject to confirmatory experimentation, could be used if other properties make them desirable for use in methanol-gasoline fuel systems.

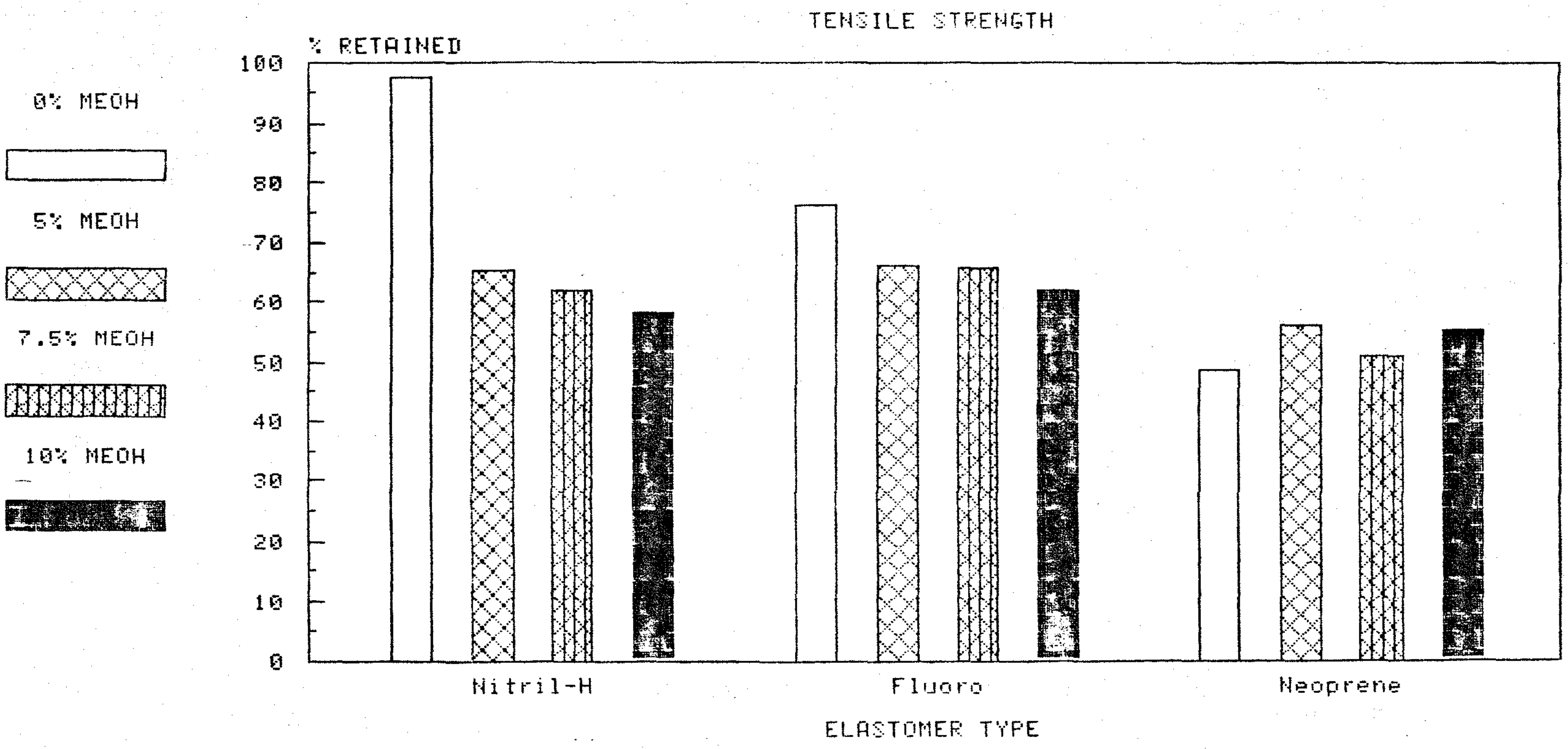

FIGURE 5. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER TENSILE STRENGTH -- PHASE II

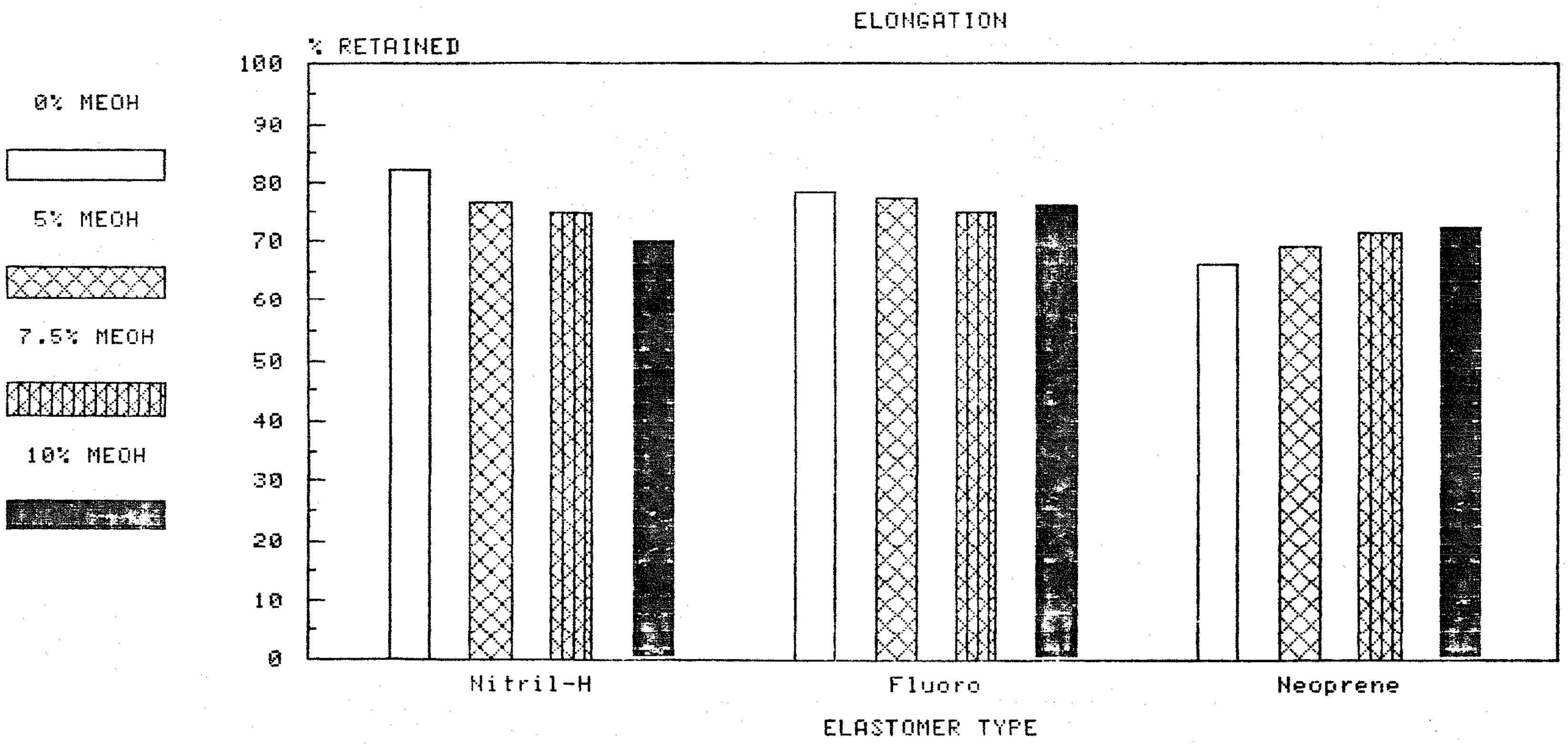

FIGURE 6. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER ELONGATION — PHASE II

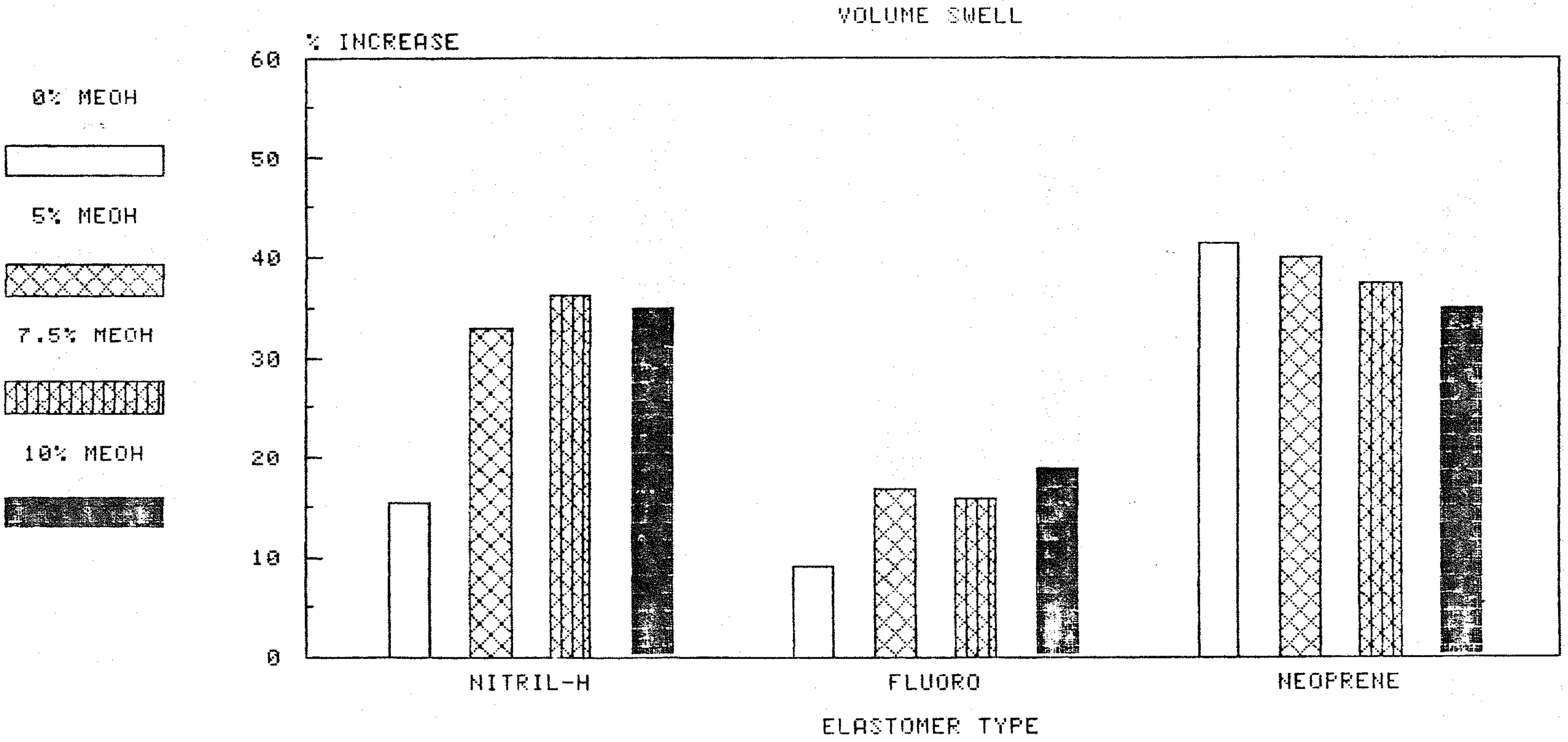

FIGURE 7. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER VOLUME SWELL — PHASE II

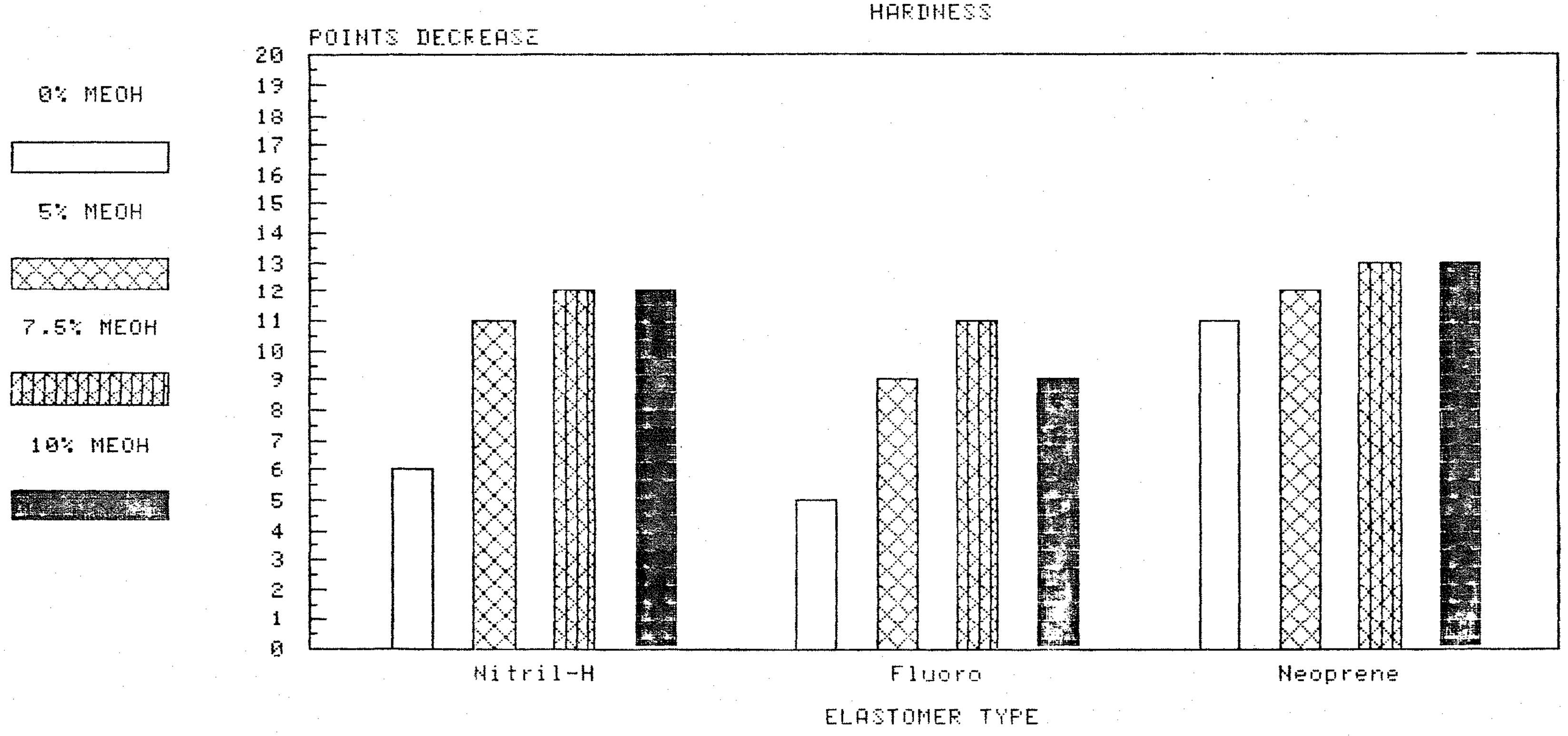

FIGURE 8. EFFECT OF METHANOL IN CONTROL SOLUTIONS ON ELASTOMER HARDNESS -- PHASE II

CONCLUSIONS

Based upon the findings of this investigation, the following conclusions pertinent to material compatibility in methanol-gasoline blends are presented:

- Additive treatment provided some metal corrosion inhibition for brass, bronze, copper, and terneplate; inhibition was inconsistent relative to methanol concentration.

- Aluminum, zinc, carbon steel, stainless steel, and cast iron were not corroded in any of the blends with or without additives over an extended test period.

- Corrosion inhibition detected was slight except in a few cases and in one case the additive effect was apparently detrimental; where protection was observed for brass and terneplate it seemed to be the result of combining two additives; increasing additive concentration above manufacturers' recommendation did not make any noticeable improvement.

- Results of short-term (30 days) corrosion testing may differ from the long-term, but if there is no corrosion evident after 30-60 days of testing, there may be no significant corrosion in a longer term test.

- Vapor phase effects with the exception of magnesium are not readily discernible on a partially immersed metal specimen used to determine solution corrosivity.

- Magnesium is quickly and destructively corroded by vapors of the 20 percent (vol) methanol blend and to a lesser but significant extent at the lower concentrations; the test additives appeared to promote the deleterious effect except for additive D which provided protection for the metal in the 20 percent (vol) methanol blend.

- Weight change and pitting are not effective measures of corrosivity under the conditions of these tests.

- No beneficial or detrimental effects attributable to the additives were observed for nonmetal material compatibility with the methanol blends.

RECOMMENDATIONS

The results of the short-term corrosivity and compatibility test program suggest the following recommendations which may aid other investigators in the study of protection of materials by additives in fuel blends containing methanol.

- Future work in characterization of protective mechanisms of corrosion control in methanol-gasoline fuel blends should concentrate on additive B, a mixture of acylated amines in aromatic hydrocarobons, and additive D, a substitued high molecular weight succinic acid, the only two formulations which gave any indication of lessening the corrosivity effects of methanol-gasoline fuels on metals.

- To make the evaluation of corrosion more meaningful and reliable, especially on a short-term or accelerated testing basis, the mechanisms of corrosion protection need to be better defined.

- Characterization of the color reactions which take place on metal coupon surfaces subjected to corrosivity testing would aid in developing a useful rating system for evaluating the extent of corrosion.

- The procedural details of testing need to be developed to aid in determining what conditions are required to determine the extent of corrosion by pitting or weight change measurements that may be extrapolated to long-term results. This should include the determination of procedures and conditions for the observation of vapor phase effects.

- Identify a list of metals and nonmetals that are representative of those used in fuel systems and should be used as standards for material testing.

REFERENCES

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16 Abstract

Additives commercially available for use in liquid handling systems were obtained and screened for application to the protection of materials used in automotive fuel systems which would be exposed to the harmful effects of methanol should it be used as a gasoline extender. Six additives were chosen to provide a diversity of applications and chemical types in order to enhance the probability of finding an effective formulation. The screening tests determined the efficacy of the additives as modifiers of methanol's corrosivity toward metals and its weakening of tensile properties of nonmetals. From the screening phase, three additives seemed to protect some of the metals; these were tested in higher concentrations and binary combinations in search of optimal application conditions. Results indicated that two of the additives have protective properties and combining them increases the protection of the metals corroded by methanol-gasoline blends. Half of the metals in the tests were not corroded. Testing at recommended concentrations and then at higher concentrations and in combinations showed that the additives would have no protective or harmful effects on the nonmetals. Two additives emerged as candidates for application to the protection of metals in automotive methanol-gasoline fuel systems. The additives tested in this program were assigned letter codes to protect their proprietary nature.

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