Table IX. Rubber-Rich Hycar—Phenolic Blends

Recipe			
Hycar 1072	100.0	100.0	.....
Hycar 1042	.....	.....	100.0
Durez 12687	25.0	50.0	50.0
Stearic acid	2.0	2.0	2.0
Zinc oxide	10.0	10.0	5.0
TMTD	.....	.....	3.5
All cures 30 minutes at 310°F.			
Ultimate tensile strength, p.s.i.	3700	3970	2350
Ultimate elongation, %	420	190	490
Hardness (Duro D)	42	58	39
Tear resistance, ASTM D 624, die C with grain, lb./inch	440	620	470
Low temperature brittleness, ASTM D 746			
Pass, °F.	−60	−25	−25
Fail, °F.	−70	−35	−35
ASTM oil 3, 70 hours at 300°F., vol. change, %	+23	+17	+19

CEMENTS

Hycar 1072 is readily soluble in the usual solvents used in making cements from nitrile rubbers. The possibility of a zinc oxide cure of a Hycar 1072 cement suggests a method of obtaining a tough, highly abrasion-resistant, unloaded film. Cements made from mixtures of Hycar 1072 and phenolic resins have shown good adhesion to metals. The presence of the reactive carboxyl group may suggest unique applications as protective coatings, caulking materials, or adhesives.

SUMMARY

The building of carboxyl groups into a nitrile polymer has changed many of the characteristics of the basic polymer from which it was built. Comparison of the carboxyl containing polymer with a similar nitrile polymer devoid of carboxyl groups leads to the following conclusions:

1. The oil and fuel resistance of the polymer is not harmed by the presence of the carboxyl groups, in fact, volume change on immersion in such materials is decreased slightly.
2. The inclusion of carboxyl groups in the nitrile polymer has produced a high gum tensile strength rubber with high oil resistance.
3. Recipes used for standard nitrile polymers are generally satisfactory with Hycar 1072.
4. When a standard nitrile polymer is compared with the carboxylic nitrile polymer in identical recipes, the carboxyl containing polymer exhibits a higher tensile strength, modulus, hardness, compression set, tear, not tensile, hot elongation, hot tear, and abrasion resistance. At the same time elongation and rebound are lower and low temperature brittleness is improved.
5. The hardness of a Hycar 1072 vulcanizate decreases more rapidly than a normal nitrile as the operating temperature rises above room temperature.
6. The use of plasticizers or reduced loading are effective methods for reducing the hardness of Hycar 1072 vulcanizates.
7. In the presence of low amounts of reinforcing agent Hycar 1072 vulcanizates retain satisfactory properties and in addition possess low temperature brittleness values near −95°F.
8. The carboxyl containing nitrile polymer shows unusual properties in blends with poly(vinyl chloride) and phenolic resins.

The properties observed suggest application in fields requiring high hardness compounds at no sacrifice in other properties; use in such items as oil well parts, shoe soles, and belting where higher abrasion resistance would be valuable; application in such lines as adhesives, protective films, and prosthetics where a high gum tensile in addition to other properties of a highly oil resistant polymer are valuable; use in conjunction with resins of various kinds of which poly(vinyl chloride) and phenolic types are typical; and adaptation to parts exposed to shock and oil or fuel at very low temperatures.

Hycar 1072 (B. F. Goodrich Chemical Co.), the carboxyl containing polymer described, is available commercially.

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Some Properties of Lignite Creosote

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The present study concerns an evaluation of properties of creosote derived from Saskatchewan lignite. Additional properties to those reported by Prostel (*8*) for North Dakota lignite have been measured. These include creosote toxicity, the effect of chlorination on the toxicity, and the rate of evaporation of the preservative.

At Bienfait, Sask., lignite is treated by the Lurgi low temperature carbonization process (*1,9*). The maximum temperature in the retort is 1290° to 1380°F. The lignite tar is condensed from the gas stream and is distilled at atmospheric pressure in batches. The fraction distilling between approximately 425° and 710°F. is collected as creosote. Two specimens were considered in the present study. The first was a representative stream sample from the distillation. The second was taken from a commercial shipment supplied to Northern Wood Preservers (Sask.) Ltd., Prince Albert, Sask.

Except as noted, the standard methods of the American Wood-Preservers' Association (*4*) were used in obtaining the data presented. Toxicity measurements were made by the agar flask method (*5*) as modified by Finholt (*7*). *Polyporus tulipiferus* (Madison 517) between 12 and 15 days old was the fungus used for inoculations.

In the initial stages of the work fractionations by distillation were made both at atmospheric pressure and under vacuum. However, as later work showed that distillation at atmospheric pressure did not adversely affect the toxicity of the preservative, vacuum distillation was discontinued.

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Table I. Properties of Creosote Specimens

Specimen	I	II
Specific gravity, 38° C./15.5° C.	0.967	...
Water content, wt. %	2.4	1.6
Distillation range[a], °C.		
I 0–210	5.0	2.2
II 210–235	21.8	10.1
III 235–270	25.9	25.5
IV 270–315	23.4	28.6
V 315–355	12.6	18.0
Residue	10.3[b]	14.9
Losses	1.0	0.7
Insoluble in benzene, wt. %	0.22	...
Coke residue[c], wt. %	0.75	...

[a] Per cents by weight on dry basis. For specimen I figures are average values for 8 distillations.

[b] Float test (*2*), 34 seconds.

[c] Standard coal crucible used.

Considerable work has been done on chlorine compounds as wood preservatives (*11*). In the present investigation chlorination was carried out by bubbling chlorine through whole creosote or its fractions in the presence of iron wire, and later washing the material with water to remove hydrochloric acid.

An evaporation curve was obtained by exposing lignite creosote in Petri dishes in a room at 23° ± 2° C., and weighing the dishes at periodic intervals up to 26 weeks.

RESULTS AND DISCUSSION

Various properties of the creosote specimens examined are listed in Table I. The specific gravity of lignite creosote is considerably less than that stipulated by ASTM standard D 390–53 (*3*). The specification for water content is met. However, water apparently formed and settled out at the bottom of creosote specimen I. If this water is included, the specification is not met. Material insoluble in benzene and coke residue falls within the stipulated limits, and the distillation range nearly falls within the limits. Similar results have been reported by Prostel (*8*) for North Dakota lignite creosote.

Table I shows that larger percentages of higher boiling material were found in specimen II than in specimen I. This result is consistent with the fact that considerable paraffin wax crystallized from specimen II at temperatures below about 40° F.

In Table II are reported the specific gravities, the tar acid contents, and the toxicity characteristics of creosote specimen I and its fractions. A few data for specimen II are included also. The apparent inhibition point (AIP) (*7*), is the lowest weight per cent of preservative in the malt-agar-creosote mixture which will prevent radial growth from the fungus transplant onto the surface of the agar mixture. The total inhibition point (TIP) (*10*), is the minimum weight per cent required to prevent visible growth on both the poisoned malt-agar and the inoculum. The killing point (KP) (*10*), is the minimum weight per cent which will kill the fungus as indicated by its failure to grow when transferred from the poisoned to an unpoisoned medium. Finholt (*7*) points out that whereas all of the above three criteria depend on the toxicity of the preservative, the total inhibition point and the killing point depend also on its diffusivity in the inoculum. Therefore the apparent inhibition point being independent of diffusivity, should be a more useful indication of toxicity. To facilitate the making of comparisons, data for each of the three criteria were obtained in the present work.

The tar acid contents are lower than those reported by Prostel (*8*) for North Dakota lignite creosote, although the pattern of distribution among the fractions is similar. The tar acid content of a mixture of fractions I to V (*4*) is less than would be expected on the basis of the individual fractions.

Table II. Specific Gravity, Tar Acid Content, and Toxicity of Creosote Specimens and Fractions

	Sp. Gr., 38° C./15.5° C.	Tar Acids, Wt.%	AIP, Wt.%	TIP, Wt.%	KP, Wt.%
Whole creosote, specimen I	0.967[a]	34[b]	0.065[c]	0.085	0.090
Whole creosote, specimen II			0.055	0.095	...
Fraction, °C., specimen I					
I 0–210	0.899	35	0.085	0.095	0.095
II 210–235	0.963	51	0.055	0.055	0.065
III 235–270	0.967	47	0.060	0.085	0.100
IV 270–315	0.968	32[b]	0.10	0.11	0.16
V 315–355	0.973	28[b]	0.095	0.165	...
Fractions I to V mixed		33	0.055	0.090	0.095

[a] For whole creosote only a Westphal balance was used.

[b] For these fractions only a gravimetric method was used in which tar. acids were isolated and weighed as such. This method gave results almost identical with those obtained by the AWPA method for fractions II, III, and IV.

[c] Where three figures are given after decimal point, toxicity values are known within approximately ± 0.005 or less.

The toxicity values for lignite creosote satisfy the arbitrary criterion of Vaughan (*12*) that a satisfactory wood preservative should have a killing point of 0.1% or less. The killing point is the same as that reported by Duncan (*6*) for creosote from Texas lignite. For the fractions of lower boiling point (and, presumably, lower average molecular weight) little difference exists between the apparent inhibition points and the corresponding killing points. However, for fractions of high boiling point, considerable difference exists between the two values because of the lower diffusion rate of the preservative in the fungus transplant. The apparent inhibition points listed in Table II show that the two distillation fractions collected between 210° and 270° C. are more toxic than the other fractions. However, Duncan (*6*) shows that the tar acids in the fractions above 270° C. are of prime importance in producing the toxicity of the creosote tested by her.

Table III. Effect of Chlorination on Toxicity

	Whole Creosote, Specimen I		Vacuum Fraction III[a]	
Av. Molecular Weight[b]	Untreated	Chlorinated	Untreated	Chlorinated
	199		162	
AIP, wt. %	0.065	0.040	0.045	0.010
TIP, wt, %	0.085	0.085	0.050	0.010
KP, wt. %	0.090	0.100	0.050	0.010

[a] Obtained by vacuum distilling lignite creosote specimen I at absolute pressure between 8 and 15 mm. of mercury. This fraction boiled between 82° and 90° C. under these conditions. Material would be found in AWPA fractions II and III.

[b] By freezing point depression method.

Table III shows the effect of chlorination on the toxicity of the whole creosote, and on that of one of the fractions from the vacuum distillation of creosote specimen I. The extent of chlorination was estimated to be one gram-atom of chlorine per gram-mole of creosote. Table III shows that chlorination has improved the toxicity of fraction III but was less effective with whole creosote.

Other effects of chlorination included an increase in the specific gravity of the preservative; for vacuum fraction III from 0.991 to 1.17. For the whole creosote the specific gravity after chlorination was not measured, but is known to exceed 1.00. Also, chlorination resulted in the formation of considerable slimy or gummy residue in the whole creosote, but not in vacuum fraction III.

In Figure 1 the results of the evaporation test for lignite creosote specimen I are compared with results of a similar test done by Vaughan (*12*) on coal-tar creosote. The purpose of these tests was to obtain some idea of the probable permanence of the preservative. From Figure 1 lignite creosote may be expected to be less satisfactory than coal-tar creosote in this respect. However, volatility effects may be offset to a degree by a possible greater ease of penetration of the wood by lignite creosote during impregnation.

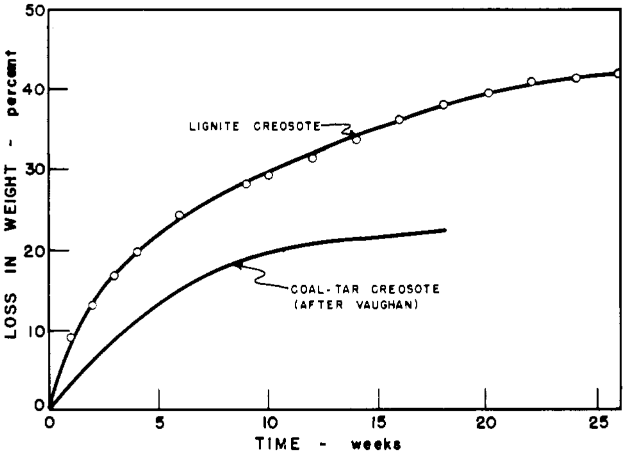

Figure 1. Evaporation curves of lignite and coal-tar creosotes

CONCLUSION

The proper evaluation of a wood preservative requires the use of service tests such as listed by Prostel (*8*) for lignite creosote. However, the toxicity values reported in the present study suggest that lignite creosote should prove to be a satisfactory wood preservative. Chlorination may enhance its usefulness, although means of eliminating sludge formation would have to be investigated.

ACKNOWLEDGMENT

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Applicability of a Specific Gravity-Oil Yield Relationship to Green River Oil Shale

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A specific gravity-oil yield relationship developed by the Bureau of Mines, Department of the Interior, for oil shales of the Rifle, Colo., area (*6*) is applicable to oil shales from 10 locations in the Piceance Creek Basin of Colorado and the Uinta Basin of Utah.

Average values of weight of oil shale per unit volume and oil yield of oil shale per unit volume based on shale specific gravities estimated from this relationship showed error limits which were less than ± 2.6% of corresponding values based on determined shale specific gravities. For all the samples included in this study the standard deviation from determined oil yield values of oil yields estimated from determined specific gravities using the D-5 relationship was 2.0 gallons per ton. This datum indicates that 95% of estimated oil yields will fall within 4 gallons per ton of the determined values. Nine of the 10 cores chosen for this study were from the Piceance Creek Basin deposit in Garfield and Rio Blanco Counties, Colo. One core was from the Uinta Basin deposit in Uintah County, Utah. These cores afford the best coverage available at present for the Green River formation oil shales as a whole.

To compare oil shales of equivalent grade, sections of the cores having average oil yields of 25 gallons of oil per ton of shale were examined. These sections represent the Mahogany zone of the Green River formation, which is comprised of the richest oil shales in the formation and will probably be the first portion processed commercially to liquid fuels. The oil shales in this zone are commonly designated by their distance above and below a distinctive bed of analcite about 4 inches thick, known as the Mahogany marker. Geologic studies indicate that the Piceance Creek Basin and the Uinta Basin were once continuous, and the oil shales in both basins show the Mahogany marker and the Mahogany zone.

The relationship between specific gravity and oil yield is a consequence of the nature of oil shale. Specific gravity varies inversely and oil yield varies directly with the concentration of organic material in the shale. The relationship for oil shales of the Green River formation is not linear, because the percentage of organic material converted to oil and the specific gravity of the oil change with the amount of organic material. However, when the specific gravities of the constituents of oil shales from a deposit are uniform over the deposit, a relationship applicable to the entire deposit may be developed (*4, 5*). In the previous study the compositions of oil-shale samples from two locations in the Green River formation were shown to be uniform enough to allow development of an algebraic equation relating specific gravity to oil yield for each of two locations (*6*). The present study demonstrates the applicability of one of these relationships developed for test hole D-5 of the Rifle, Colo., area to nine other cores and, by implication,