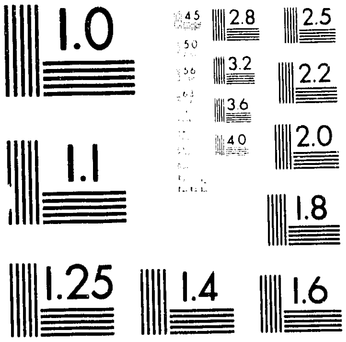
1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

1 of 1

DOE/MC/11076-3410
(DE93011306)

Evaluation of Energies of Interaction Correlated With Observed Stabilities and Rheological Properties of Asphalt-Aggregate Mixtures of Western Shale-Oil Residue as a Modifier to Petroleum Asphalt

Topical Report

J. E. Tauer
E. K. Ensley
P. M. Harnsberger
R. E. Robertson

February 1993

Work Performed Under Contract No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Wyoming
Western Research Institute
Laramie, Wyoming

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161; phone orders accepted at (703) 487-4650.

DOE/MC/11076-3410
(DE93011306)
Distribution Category UC-123, 126

Evaluation of Energies of Interaction Correlated With Observed Stabilities and Rheological Properties of Asphalt-Aggregate Mixtures of Western Shale-Oil Residue as a Modifier to Petroleum Asphalt

Topical Report

J. E. Tauer
E. K. Ensley
P. M. Harnsberger
R. E. Robertson

Work Performed Under Contract No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
University of Wyoming
Western Research Institute
P.O. Box 3395
Laramie, Wyoming 82071

February 1993

TABLE OF CONTENTS

SUMMARY

The objective of this study was to perform a preliminary evaluation of improving bonding and aging characteristics using a distillation residue from the Green River Formation (western) shale oil as a modifier to a petroleum asphalt for use as a crack and joint filler material in portland cement concrete and asphaltic pavements. This study was to examine the differences in moisture damage resistance and adhesion properties, as measured by bonding energy, of shale-oil modified asphalts compared with non-modified asphalts. The shale-oil modified asphalts mechanical properties were not expected to match those of the rubberized asphalt. A commercially available rubberized asphalt crack and joint filler material was also tested only for comparison of mechanical properties. Portland cement concrete briquets prepared with an asphalt material sandwiched between two concrete wafers were tested in a stress-relaxation type of experiment to evaluate the relaxation and recovery properties of the sealant materials. Energy of interaction (bonding energy) measurements were performed on asphalt materials with portland cement concrete, two silicate aggregates, and a limestone aggregate to evaluate the compatibility of the asphalt materials with various aggregates. The results show that the shale-oil modified petroleum asphalt improved the relaxation time, percent recovery, and bonding energy compared with the petroleum asphalt.

INTRODUCTION

In the United States today, there are over 2 million miles of paved roads (The Asphalt Institute 1989). There has been much national attention focused on the decay of the transportation infrastructure of the United States, and more specifically, the decay of roads and bridges. Some 30 billion dollars are spent annually by the states and federal government to maintain, reconstruct, and construct highways. It is not uncommon for major highway reconstruction costs to be $1 million or more per mile of highway. Therefore, it is of paramount importance to properly maintain and repair the roadways that are currently performing to an acceptable level; thus, extending their useful lifetime and delaying the very costly reconstruction process.

All highways, regardless of whether the material is asphalt concrete or portland cement concrete, suffer from cracking during their useful lifetime of service. Cracking can be caused by a variety of problems, some of which are thermal expansion and contraction, moisture, repeated heavy loads, or inadequate subgrade. In addition to cracking, portland cement concrete pavements have sawed joints at specific intervals to help relieve stresses that normally occur during service. Cracks and joints provide an access point for surface water to enter the subgrade and cause pavement damage by a loss of structural strength of the subgrade. Water entering through a crack or joint in a pavement also increases the likelihood that the pavement will suffer from moisture damage. Most pavement engineers tend to underestimate the amount of surface water that can enter the structural section from above (Hogan 1980). Another problem that can occur as a result of unsealed cracks or joints is the invasion of dirt. Regarding pavement deterioration from unsealed joints, Wolters (1974) stated that the most noticeable problem is joint spalling caused by the infiltration of water and incompressibles into the joints. As foreign material accumulates in the joint and when an increase in ambient temperature causes the joint to close, tremendous pressures build up, which can induce "blow ups" and joint spalling.

Currently, rubberized asphalt is used as a crack and joint filler, but because of its high cost, other materials are being investigated. This study investigates the rheological properties of shale-oil modified asphalts and the compatibility of shale-oil modified asphalt and selected aggregates for possible use as a crack and joint filler. Rheological properties such as the viscous and elastic moduli, relaxation time, and percent recovery are used to predict the temperature susceptibility (the rate at which the rheological properties change with temperature) of an asphalt. Temperature susceptibility indicates how an asphalt behaves over a range of temperatures. If the asphalt has a high temperature susceptibility the pavement or filler made with this asphalt is likely to also have a high temperature susceptibility. The compatibility of an asphalt and aggregate can be determined by the energy of interaction (bonding energy) given off during mixing. The more exothermic the reaction, the more compatible the materials are. Also, higher bonding energy should relate to better resistance to moisture damage. These two properties are useful in predicting the success of a material as a crack and joint filler, and of pavements constructed with these materials.

In an earlier report (Harnsberger et al. 1992), it was found that the shale-oil modified asphalts did not pass the very severe ASTM D 3407 extension test. However, the shale-oil modified asphalts showed better adhesion and resilience in the extension test compared with the AC-20 asphalt.

EXPERIMENTAL

Materials

Shale-Oil Modifier

The western shale-oil modifier (a proprietary product) was prepared by and obtained from the New Paraho Corporation. It was produced by a proprietary process from Green River Formation oil shale. The whole shale oil was vacuum distilled to produce a +371 °C (+700 °F) residue, then further processed by a proprietary method to produce a specification-grade AC-20 asphalt that was used as the modifier in this study.

Petroleum Asphalt

The petroleum asphalt was obtained from the Sinclair refinery in Sinclair, Wyoming and was an AC-20 grade.

Rubberized Asphaltic Material

The rubberized asphaltic material used for comparison purposes was obtained from a commercial supplier and was a standard specification-grade crack and joint filler material.

Concrete

Portland cement concrete used for slab-joint simulations was prepared according to ASTM Procedure C 192.

Aggregates

Aggregates used for bonding energy measurements were crushed portland cement concrete, two silicates referred to by the Strategic Highway Research Program (SHRP) as RL silicate and RJ silicate, and a dolomitic limestone.

Procedures

Preparation of Portland Cement Concrete Test Specimen

Concrete slabs 30.48 cm square and 7.62 cm thick were poured and finished. They were covered with plastic and cured in a 100% humidity chamber for 25 days. The forms were removed after 48 hours. Concrete disks were prepared by coring portland cement concrete slabs using a carbide-tipped coring tool measuring 4.45 cm in diameter. The cores were then sawed into 1.27 cm slices using a water-cooled masonry saw equipped with a diamond-impregnated blade. After sawing, the disks were stored in a saturated lime water solution until used.

Preparation of Aggregates

Preparation of portland cement concrete aggregate was performed by crushing pieces of the concrete slab and sieving the crushed concrete to obtain a - 35+48 mesh fraction using Tyler sieves. Silicate and limestone aggregates were prepared by crushing pieces of the aggregate rock and sieving the crushed rock to obtain a - 35+48 mesh fraction using Tyler sieves.

Preparation of Shale-Oil Modified Asphalts

Blends of 10 and 20 wt % shale-oil modifier with AC-20 asphalt were prepared by weighing the appropriate amounts of each constituent into quart cans. The total amount of each mixture prepared was 800 grams. The empty space remaining in each can was purged with argon gas. Then the cans were heated at 150°C (302°F) for 5 hours in an oven. The cans were removed from the oven every hour and shaken in a paint shaker for a period of 5 minutes. After 5 hours, the oven was turned off, and the mixtures were allowed to cool to room temperature overnight.

Microcalorimetry

The microcalorimeters used have been described previously in the literature (Ensley and Scholz 1972). In this study,the microcalorimeters were operated at a temperature of 160°C (320°F). Approximately 3 grams of aggregate, -35+48 Tyler mesh size, were placed in a small cylindrical cell which was then immersed in a larger cell containing asphalt. A Teflon^{TM} trap door separated the aggregate from the asphalt. The cell assembly was then placed in the calorimeter and allowed to come to temperature overnight. The trap door was then sprung open, allowing the asphalt and aggregate to interact. The released interaction energy was detected by the microcalorimeter, amplified, and recorded. The rate of energy released and/or the total energy released over a given time period was calculated from calibration curves.

Pressure Aging

The asphalt samples were heated and mixed with a paddle stirrer at 150°C (302°F) for 6 hours in an oven to simulate day-long heating in a hot-applicator pot. Then 7.89 grams of asphalt were weighed into a small pan, 5.4 cm in diameter and 0.7 cm deep. This amount of sample produced a film thickness of 0.318 cm. The treated, prepared samples were then placed into the pressure-aging vessel (PAV).

The PAV is cylindrical, approximately 19.05 cm i.d. and 19.05 cm in height. The vessel was filled with air to achieve a pressure inside the vessel of 2.07×10^6 Pa (300 psi) at reaction temperature. The vessel and contents were placed in a VWR 1630 forced-draft oven. The temperature of the oven was adjusted to produce a temperature of 70°C (158°F) inside the PAV as measured by a thermocouple placed inside the vessel. After 144 hours the PAV was slowly vented, removed from the oven, and cooled. The oxidized asphalts were stored in sealed plastic bags in pans until used for rheological measurements.

Annealing

Annealing of the unaged samples was performed by weighing 5 to 6 grams of sample into a small vial and purging with argon. The samples were then placed in an oven at 150°C (302°F) for 1 hour. The samples were removed from the oven and allowed to cool to room temperature for 0.5 hour. Rheologic measurements were then made.

The aged samples were annealed for one hour at 70°C (158°F) under vacuum with an argon gas purge. Samples were removed and allowed to cool to room temperature for 0.5 hour. Rheologic measurements were then made.

Rheological Testing of Asphalt

The viscosity and shear moduli of the aged and unaged material were determined on a Rheometrics mechanical spectrometer, Model RMS-605. Measurements were made in both the dynamic and transient modes at three temperatures: 60, 25, and 10°C (140, 77, and 50°F), using parallel plates spaced 2.0 mm apart (diameter varied according to sample hardness). Rheological data in the transient mode were also collected at 0°C (32°F). For the dynamic viscosity measurements, a shear frequency of 0.1 to 100 rad/sec was used with a strain setting that varied according to sample stiffness. Transient viscosity measurements were performed using the dynamic step-strain mode. In the transient experiments, the sample was torqued to a degree determined by the initial strain setting (varied according to sample stiffness) and then allowed to relax for 250 seconds. Stress and relaxation time were then calculated from the measured data.

Preparation of Portland Cement Briquets

A circular Teflon form was placed around one concrete disk. A sample of asphalt was heated to 140°C (284°F) in an oven for approximately 20 minutes or until fluid. The asphalt sample was then poured into the form to a depth of 0.5 cm and allowed to cool to room temperature overnight. The following morning, the form was removed from the sample. A second concrete disk was heated in a 140°C (284°F) oven for 5 minutes, removed from the oven, and placed on top of the asphalt portion of the previously prepared sample. The completed briquet was allowed to cool to room temperature for 1 hour. The briquet was then trimmed to remove excess asphalt and placed in the temperature chamber of the Brabender Rheotron.

Rheological Testing of Briquets

The portland cement concrete-asphalt briquets were mounted into a Brabender Rheotron. The briquets were conditioned at the test temperature 25°C (77°F) for at least 1 hour before commencing the test. The briquets were conditioned at the lower test temperatures (0 and 10°C) (32 and 50°F) for at least 2 hours. A constant torque was applied to one of the concrete disks and the transmitted or resultant torque on the second concrete disk was recorded on a strip-chart recorder. Torque was applied until a constant slope was recorded and then held in that relative position until the transmitted torque decayed to zero or near zero. Rheologic properties (relaxation time and percent recovery) were then calculated from the recorded curve.

RESULTS AND DISCUSSION

Energies of Interaction (Bonding Energy)

A necessary condition for an asphalt to be compatible with an aggregate is that a strong bond exist between the asphalt and aggregate. The relative bond strength between asphalt and aggregate can be evaluated during bond formation or after the bond has formed. In this study, bonding energy was measured during the formation of the bond, based on the premise that the stronger the bond the greater the bonding energy. A stronger bond between the asphalt and the aggregate relates to better moisture damage resistance and better adhesion. There are other methods to evaluate moisture damage resistance but they were not used in this study.

The bond between the asphalt molecules and an aggregate surface probably occurs through polar asphalt molecules interacting with ionic sites on the aggregate surface. Typical polar asphalt molecules contain heteroatoms such as nitrogen, sulfur, and oxygen. The composition of a typical western shale oil and 538°C+ (1000°F+) residue is shown in Table 1. The elemental content of the shale-oil modifier used in this study was not determined. However, it is not expected to be much different than the residue composition shown in Table 1.

A typical asphalt usually has between 2 to 5% sulfur and 0.5 to 1.1% nitrogen. The higher nitrogen in shale oil, particularly in the residue, is primarily pyridinic material which has been shown to enhance the bonding properties of asphalt modified with shale oil (Plancher and Petersen 1984).

Two important properties of asphalts used to fill cracks and joints are: (1) that the asphalt bonds well to the sides of the cut, and (2) that the rheological properties of the asphalt show a high percentage of recovery from applied stress at both low and high temperatures. The second property is also important for asphalt used in pavements. The results of bonding energy measurements on four asphalts mixed with four aggregates are shown in Table 2. The silicate and limestone aggregates represent silicate and limestone rocks exposed when a cut is made through a portland concrete roadway.

Bonding energies between asphalts and aggregates are dependent on both the number of sites per unit weight of material and the strength per site. The number of sites per unit weight is dependent on both the surface area and site density. Since the surface areas of the aggregates were not determined in this work, the comparisons will be made principally between different asphaltic materials with different aggregates. For example, examination of the bonding energies with concrete indicate that the addition of the shale-oil modifier to the control asphalt improves bonding. However, for certain aggregates (e.g., RJ silicate), the addition of 20% shale-oil modifier may be too much. The rubberized asphalt, a commercial material used as a crack and joint sealant, showed even better bonding characteristics. Higher bonding energies relate to better adhesion to aggregate surfaces and also to better resistance to moisture damage.

Bonding to limestone was not improved greatly by addition of shale-oil modifier to the asphalt. The basic nitrogen compounds in shale oil, pyrrolic and 2-quinolonic (Plancher and Petersen 1984), perhaps do not improve bonding to basic limestone where there are few acidic sites. However, the rubberized asphalt again had a considerably higher bonding energy than the control asphalt or shale-oil modified asphalts.

Relaxation Time and Recovery of Asphalt-Aggregate Mixtures

Asphaltic materials used to fill cracks in both asphaltic and portland cement concrete pavements need to possess good rheological properties.

Perhaps the most important rheological property of an asphalt crack filler is a low temperature susceptibility with respect to both viscous and elastic moduli. A material with optimum viscous and elastic temperature susceptibilities would be able to relieve stresses at low temperatures and yet not flow excessively at higher temperatures.

The rheological properties that were determined in this study are viscosity, shear moduli, percent recovery, and relaxation time. These properties were measured at 60°C (140°F), 25°C (77°F), 10°C (50°F), and 0°C (32°F) to determine temperature susceptibility. The results are shown in Tables 3, 4, and 5. During the course of the project, it was determined that the AC-20 shale-oil modifier blends were too inviscid at 60°C (140°F) for the briquet measurements to be obtained. Therefore, only the lower three temperatures were employed to make the stress-relaxation measurements. The same rheological measurements were determined on the four asphaltic materials after artificial aging using the pressure-aging vessel. When the vessel was opened, the samples displayed evidence of some frothing caused by escape of dissolved gases from the asphalt samples. This observation is a common occurrence after pressure aging and this is the reason for the annealing procedure used to coalesce the samples before rheological properties are measured. Rheological properties of briquets were also obtained at three temperatures (0, 10, and 25°C) (32, 50, and 77°F). The briquet properties evaluated included relaxation time and percent recovery. These experiments allowed for evaluation of the rheological properties of the asphaltic materials when in contact with portland cement concrete.

Figures 1 and 2 show the plots of elastic modulus (G') versus temperature for both the unaged and aged materials, respectively. These data are measured at 1 rad/sec shear frequency. The AC-20, the AC-20 + 10% shale-oil modifier, and the AC-20 + 20% shale-oil modifier curves are grouped together, but the AC-20 + 20% shale-oil modifier shows a small decrease in temperature susceptibility. The optimum line in this plot would be a lower G' at 10°C (50°F) and a higher in G' at 60°C (140°F), i.e., a smaller slope. Lower temperature susceptibility corresponds to retaining elasticity at both temperature extremes. A large G' at cold temperatures would indicate a brittle material. The addition of 10% and 20% shale-oil modifier to the AC-20 lowered the G' at 10°C. The AC-20 + 20% shale-oil modifier shows an increased G' at 60°C (140°F) compared with the AC-20. This trend is also shown for the aged samples in Figure 2, although the values for G' have increased because of aging. The aged AC-20 + 20% shale-oil modifier again shows a somewhat better temperature susceptibility at higher temperatures. Figures 3 and 4 show the viscous modulus (G") versus temperature for unaged and aged samples, respectively. Again, a lower slope, achieved by higher viscous modulus at 60°C (140°F) and a lower viscous modulus at 10°C (50°F) would be more beneficial. In Figure 3, the viscous moduli for the unaged materials show relative relationships for the AC-20 and the shale-oil modified blends similar to that for the elastic moduli. In Figure 4, the aged AC-20 + 20% shale-oil modifier exhibits a slightly better temperature susceptibility, compared with the AC-20 and the 10% shale-oil modifier blend. However, the overall trend is the same as Figure 3. Figures 5 and 6 show dynamic viscosity versus temperature for unaged and aged samples, respectively. The same trends are observed in these plots as were shown in the plots of G' and G". The addition of the shale-oil modifier lowers the viscosity regardless of aging. The plots shown in Figures 7 and 8 are relaxation time versus temperature for unaged and aged samples, respectively. The relaxation time of the Maxwell Model is derived from the stress-strain rate relation:

$$d\varepsilon/dt = d\sigma/dt\ (1/R) + \sigma/\eta \qquad (1)$$

Where ε is the strain, t is the time, σ is the stress, R is the elastic modulus, and η is the viscosity. The stress-time relation under given strain input can be found by solving the differential equation (1) above. If a constant strain is applied at time, t = 0, and the initial value of the stress σ_0 is known, the stress response can be found by integrating for these initial conditions resulting in:

$$\sigma(t) = \sigma_0(\exp - Rt/\eta) \qquad (2)$$

Equation 2 above describes the stress relaxation for a Maxwell Model under constant strain (Jaeger and Cook 1969). The rate of stress change is given by the derivative of equation 2:

$$d\sigma(t)/dt = -(\sigma_0 R/\eta)\ (\exp - Rt/\eta) \qquad (3)$$

The initial stress rate at t = 0+ (where the 0+ is commonly used to indicate the time just after application of the strain) is $d\sigma/dt = -(\sigma_0 R/\eta)$. The relaxation equation for a continuously decreasing stress is of the form:

$$\sigma = -(\sigma_0 R/\eta) + \sigma_0 \qquad (4)$$

The stress would reach zero at time, $t_r = \eta/R$, which is the relaxation time of the Maxwell Model. Most of the relaxation of stress occurs before time t because of the exp $-t/t_r$ term. The time at which the stress reaches 1/e times its initial value is called the relaxation time. The relaxation time is an indication of the ability of the material to return to its original shape. The AC-20 and the shale-oil modified blends return to zero stress, i.e., all the stress input into the system is relieved. The rubberized asphalt used for reference in the experiments does not return to a zero stress state because of cross-linking in the rubber. Some stress remains in the rubberized samples except at very high temperatures. In the stress relaxation experiments, a short relaxation time at 0°C (32°F) and a longer relaxation time at 60°C (140°F) is desirable. In the unaged case, the AC-20 + 20% shale-oil modifier blend shows a better relaxation time compared with the AC-20 and the AC-20 + 10% shale-oil modifier. This trend is repeated in the aged plot but is much more noticeable. The AC-20 + 20% shale-oil modifier has a much shorter relaxation time at 0°C (32°F) indicating some flow, but at 60°C (140°F) the AC-20 and the shale-oil modified blends all have approximately the same relaxation times.

The rheological data from the briquet testing are shown in Table 5. Relaxation time and percent recoveries are plotted versus temperature in Figures 9 and 10, respectively. The samples for the briquet experiments are unaged samples only. In Figure 9 the AC-20 + 20% shale-oil modifier shows the fastest overall relaxation time and therefore has also retained the greatest amount of elastic component, or the viscous component has increased at all temperatures. The relaxation times shown for briquets are calculated in the same manner as the neat asphalt relaxation times, but the initial stress is much larger in the briquet testing. Figure 10 shows the percent recovery of rheological properties versus temperature. As was stated above, the rubberized material does not return to zero stress but retains some stress even at 60°C (140°F). The AC-20 and the shale-oil modified blends return to zero stress and this is reflected in Figure 10 by the high percent recoveries (<95%) at 60°C (140°F). The percent recoveries of rheological properties for the AC-20 and the shale-oil modified blends are also high at 25°C (77°F). Again, the AC-20 + 20% shale-oil modifier shows better results compared with the AC-20 and AC-20 + 10% shale-oil modifier by having a higher recovery of rheological properties at 0°C (32°F).

The dynamic mechanical analysis and the briquet data indicate a slight improvement in performance with the shale-oil modifier. However, it appears the improvement does not occur until at least 20% shale-oil modifier has been added.

CONCLUSIONS

The addition of shale-oil modifier to AC-20 asphalt did not result in a major improvement in properties compared with an unmodified AC-20. The bonding energy measurements and the rheologic measurements show a minor improvement with the shale-oil modifier. The increase of bonding energy with the shale-oil modified asphalts indicate an increased resistance to water stripping when used in asphalt pavement, and better adhesion to cuts in portland cement concrete and asphaltic pavements when used as a crack and joint filler. The shale-oil modified asphalts were not expected to be comparable to the mechanical properties of rubberized asphalt.

ACKNOWLEDGMENTS

The authors express thanks and appreciation to the U.S. Department of Energy for funding this work under Cooperative Agreement Number DE-FC21-86MC11076. Appreciation is also extended to the following people at Western Research Institute who contributed to the completion of this project: Mary Aldrich, Deborah Colgin, Alisa Gwin, Felicia Reid, and Janet Wolf.

DISCLAIMER

REFERENCES

Ensley, E.K., and H.A. Scholz, 1972, A Study of Asphalt-Aggregate Interactions by Heat of Immersion. J. Inst. Petrol., 58: 95.

Harnsberger, P.M., J.M. Wolf, and R.E. Robertson, 1992, Evaluation of Western Shale-Oil Residue as an Additive to Petroleum Asphalt for Use as a Pavement Crack and Joint Sealant Material. Laramie WY, WRI Report to DOE, WRI-92-R049.

Hogan, R.A., 1980, Preventative Maintenance Methods for Highway Pavements. New Hampshire Department of Public works and Highways. Paper presented at Pothole Workshop, U.S. Army Cold Regions Research and Engineering Laboratory.

Jaeger, J.C., and N.G.W. Cook, 1969, Fundamentals of Rock Mechanics, Chapman and Hall LTD and Science Paperback, London.

Plancher, H., and J.C. Petersen, 1984, Nitrogen-Containing Components from Shale Oil as Modifiers in Paving Applications. Preprints, Division of Petroleum Chemistry, American Chemical Society, 29(1): 229-237.

The Asphalt Institute, 1989, The Asphalt Handbook. The Asphalt Institute Manual Series No. 4. MS-4, p.7.

Wolters, R.D., 1974, Field Evaluation of Joint Seal Materials, Final Report. Minnesota Department of Highways.

APPENDIX

Tables and Figures

LIST OF TABLES AND FIGURES

Table **Page**

Figure **Page**

Table 1. Composition of Typical Shale Oil and Residue, %

Element	Shale Oil	Residue[a]
Carbon	84.3	83.9
Hydrogen	12.0	11.6
Nitrogen	1.7	2.4
Sulfur	1.1	1.0
Oxygen	0.9	1.1

[a] 1000°F + vacuum equivalent

Table 2. Bonding Energies[a] for Four Asphalts with Four Aggregates

	Aggregate			
Asphalt	Concrete	Limestone	RL	RJ
AC-20	134	136	178	96
AC-20 + 10% Shale-Oil Modifier	247	157	213	134
AC-20 + 20% Shale-Oil Modifier	203	174	267	64
Commercial Rubberized Asphalt	446	481	321	407

[a] Bonding energies are in units of millicalories per gram of aggregate per 2 hours bonding.

Table 3. Rheological Measurements of Unaged Samples, at 1 rad/sec

Asphalt	Temperature °C	Dynamic Viscosity dynes/cm^2	Elastic Modulus (G') dynes/cm^2	Viscous Modulus (G") dynes/cm^2	Relaxation Time seconds
AC-20	0	--	--	--	0.525
	0	--	--	--	0.526
	10	5.84E+07	3.48E+07	4.69E+07	0.324
	10	6.05E+07	3.56E+07	4.89E+07	0.326
	25	1.16E+06	4.30E+05	1.55E+06	0.140
	60	2.203+03	3.46E+01	2.20E+03	0.100
	60	2.17E+03	3.01E+01	2.17E+03	0.150
AC-20 + 10% Shale-Oil Modifier	0	--	--	--	0.585
	10	3.56E+07	2.11E+07	2.86E+07	0.357
	25	1.14E+06	3.48E+05	1.08E+06	0.150
	25	1.13E+06	3.37E+05	1.07E+06	0.132
	60	1.68E+03	2.53E+01	1.68E+03	0.140
AC-20 + 20% Shale-Oil Modifier	0	--	--	--	0.510
	10	3.10E+07	1.91E+07	2.45E+07	0.305
	25	8.90E+05	3.08+E05	8.36E+05	0.160
	60	1.58E+03	4.77E+01	1.58E+03	0.290
	60	1.53E+03	6.85E+01	1.53E+03	
Commercial Rubberized Asphalt	0	--	--	--	0.330
	0	--	--	--	0.320
	10	1.81E+06	1.20E+06	1.36E+06	0.342
	10	1.79E+06	1.21E+06	1.32E+06	0.368
	25	4.06E+05	2.87E+05	2.87E+05	0.440
	60	2.95E+04	1.79E+04	2.34E+04	1.860

Table 4. Rheological Measurements of Aged Samples, at 1 rad/sec

Asphalt	Temperature °C	Dynamic Viscosity dynes/cm^2	Elastic Modulus (G') dynes/cm^2	Viscous Modulus (G") dynes/cm^2	Relaxation Time seconds
AC-20	0	--	--	--	2.380
	0	--	--	--	2.790
	10	2.06E+08	1.67E+08	1.20E+08	1.410
	10	2.60E+08	2.13E+08	1.49E+08	1.500
	25	1.72E+07	9.60E+06	1.43E+07	1.020
	60	2.55E+04	2.42E+03	2.54E+04	0.240
	60	2.91E+04	3.03E+03	2.90E+04	0.260
AC-20 + 10% Shale-Oil Modifier	0	--	--	--	2.260
	10	1.51E+08	1.22E+08	8.97E+07	1.290
	25	1.19E+07	6.89E+06	9.77E+06	0.585
	25	1.47E+07	8.67E+06	1.19E+07	0.883
	60	2.31E+04	2.96E+03	2.29E+04	0.282
AC-20 + 20% Shale-Oil Modifier	0	--	--	--	1.600
	10	1.69E+08	1.39E+08	9.54E+07	1.680
	25	1.40E+07	8.86E+06	1.09E+07	1.520
	60	3.54E+04	6.25E+03	3.49E+04	0.863
	60	3.45E+04	6.00E+03	3.40E+04	0.290
Commercial Rubberized Asphalt	0	--	--	--	
	0	--	--	--	0.854
	10	1.28E+07	9.43E+06	8.70E+06	1.220
	10	1.60E+07	1.19E+07	1.07E+07	1.150
	25	1.90E+06	1.24E+06	1.30E+06	1.180
	60	7.48E+04	5.43E+04	5.13E+04	0.813

Table 5. Rheological Measurements of Briquets

Temperature °C	AC-20 Relaxation Time, sec	AC-20 Percent % Recovery	10% Shale-Oil Modifier + AC-20 Relaxation Time,sec	10% Shale-Oil Modifier + AC-20 % Recovery	20% Shale-Oil Modifier + AC-20 Relaxation Time,sec	20% Shale-Oil Modifier + AC-20 % Recovery	Rubberized Asphalt Relaxation Time,sec	Rubberized Asphalt % Recovery
0	262	35	280	49	262	40	73	58
0	281	41	309	26	224	62	64	56
10	132	76	88	91	72	91	112	54
10	180	83	154	86	90	88	108	49
25	14	92	20	95	10	99	54	47
25	20	98	12	98	6	98	86	53

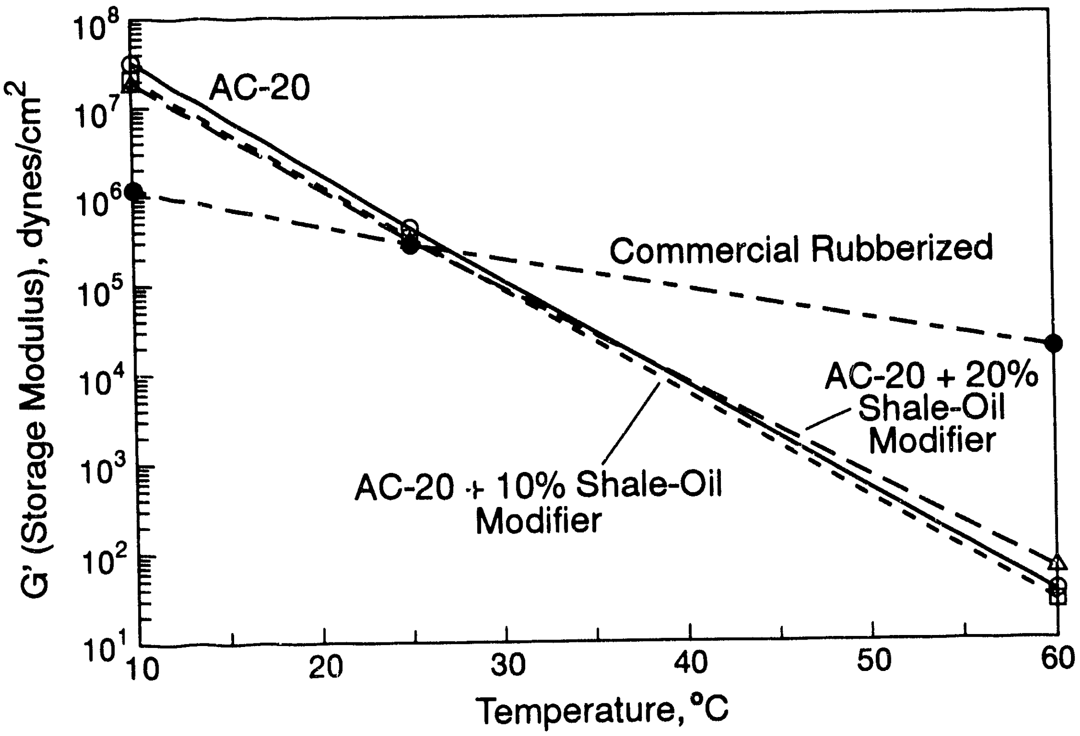

Figure 1. Elastic Modulus of Unaged Samples versus Temperature

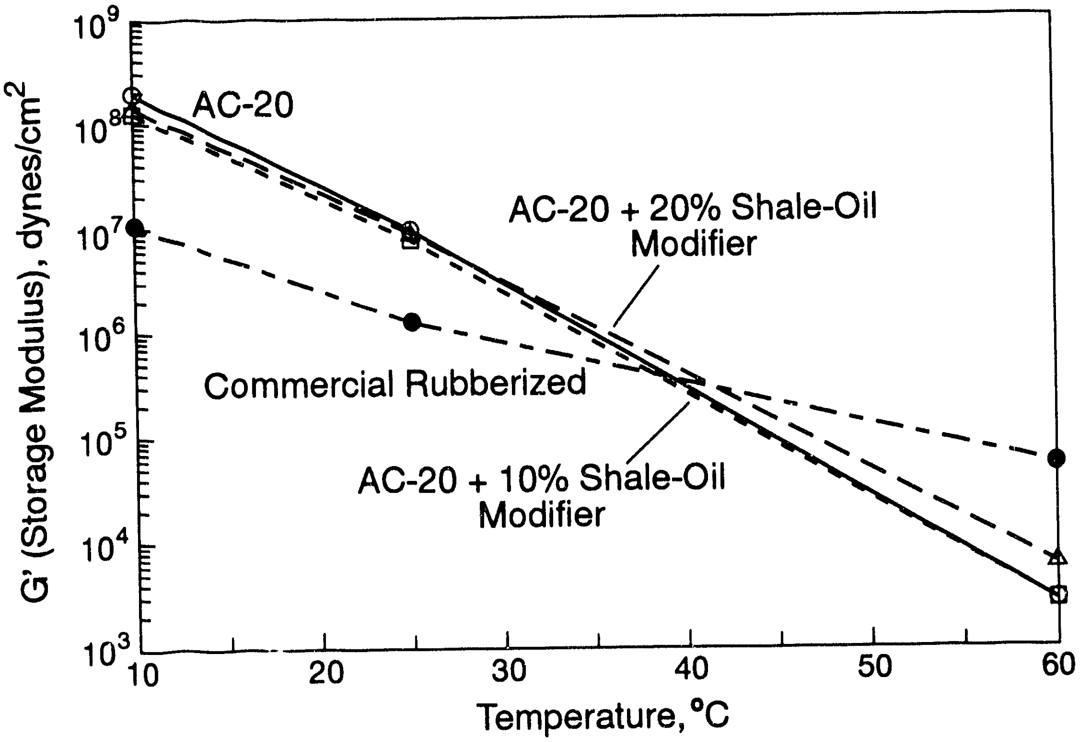

Figure 2. Elastic Modulus of Aged Samples versus Temperature

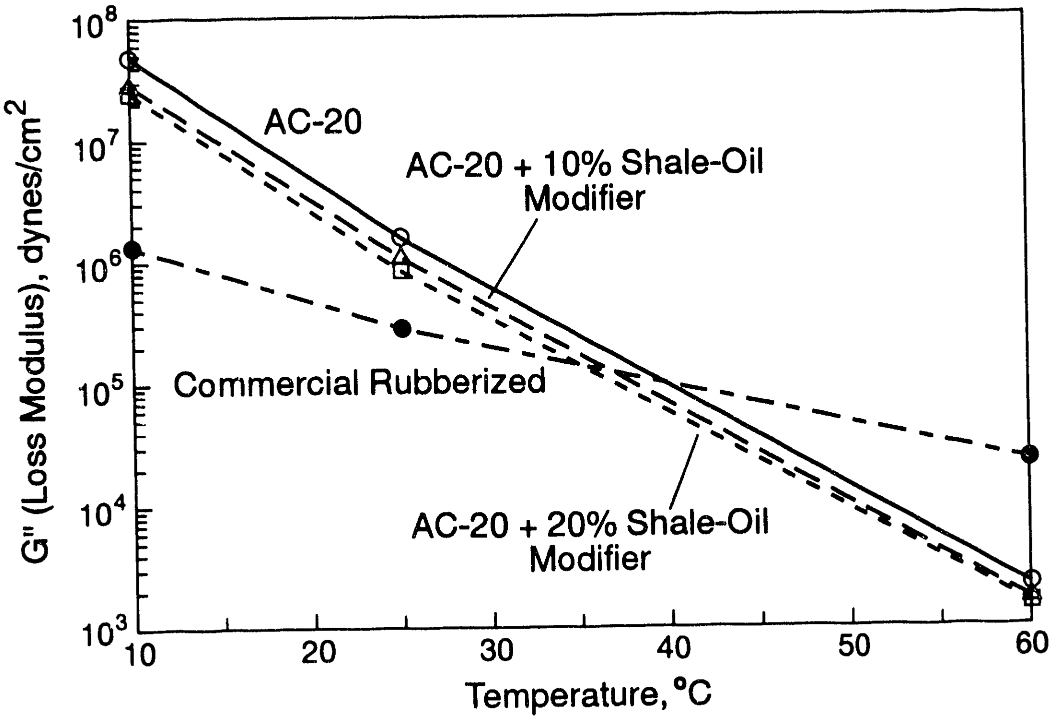

Figure 3. Viscous Modulus of Unaged Samples versus Temperature

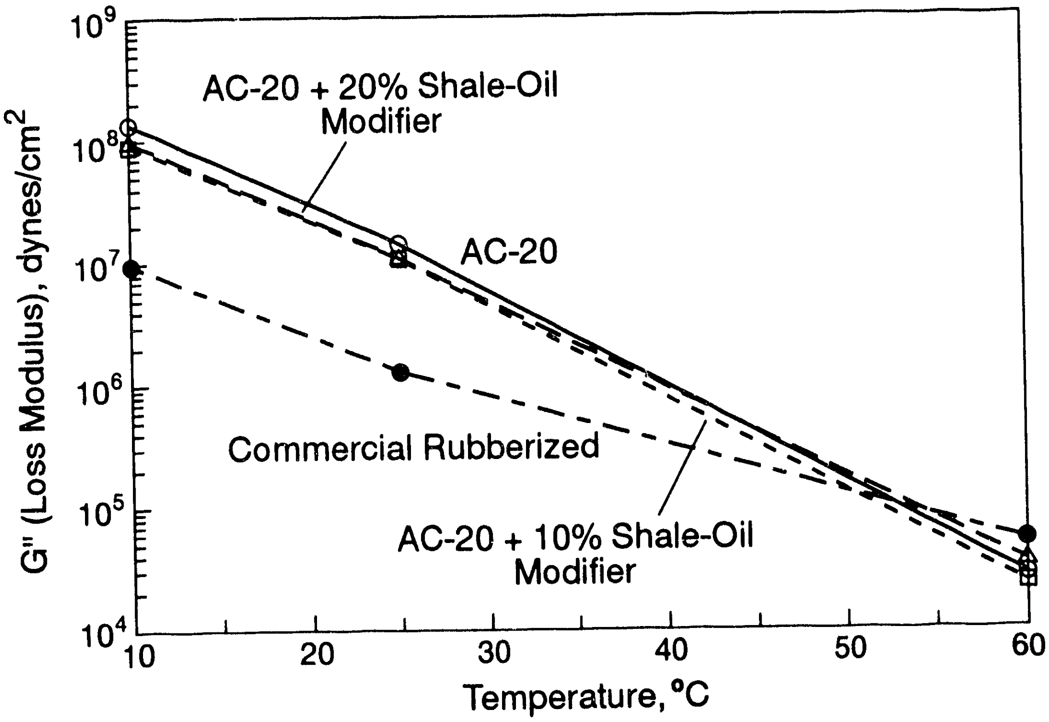

Figure 4. Viscous Modulus of Aged Samples versus Temperature

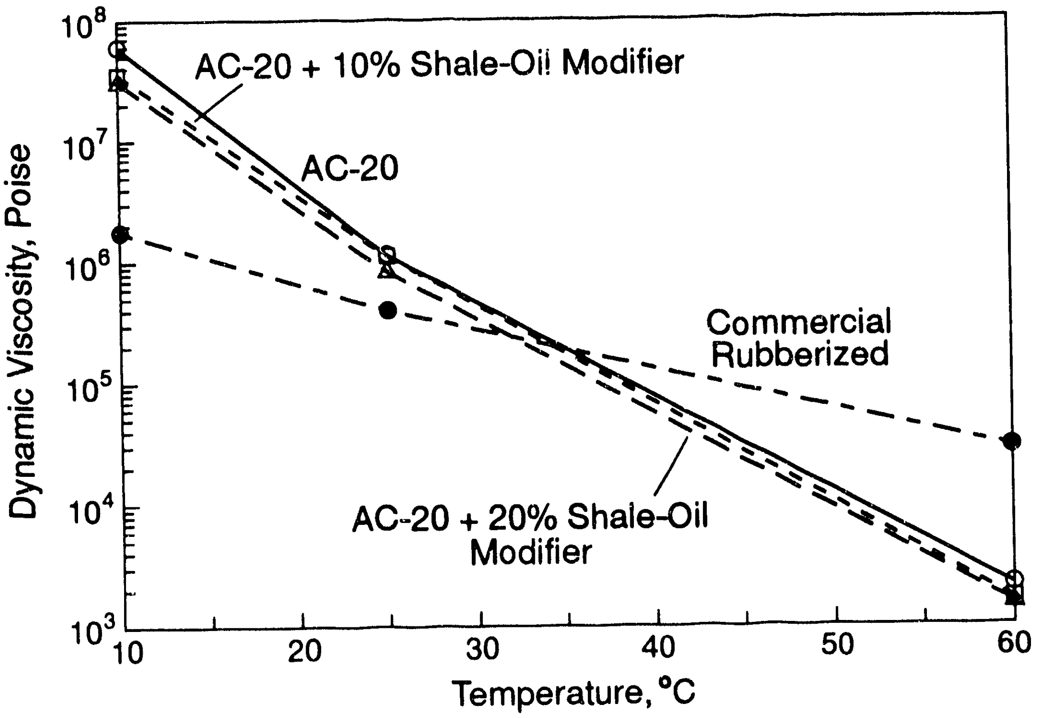

Figure 5. Dynamic Viscosity of Unaged Samples versus Temperature

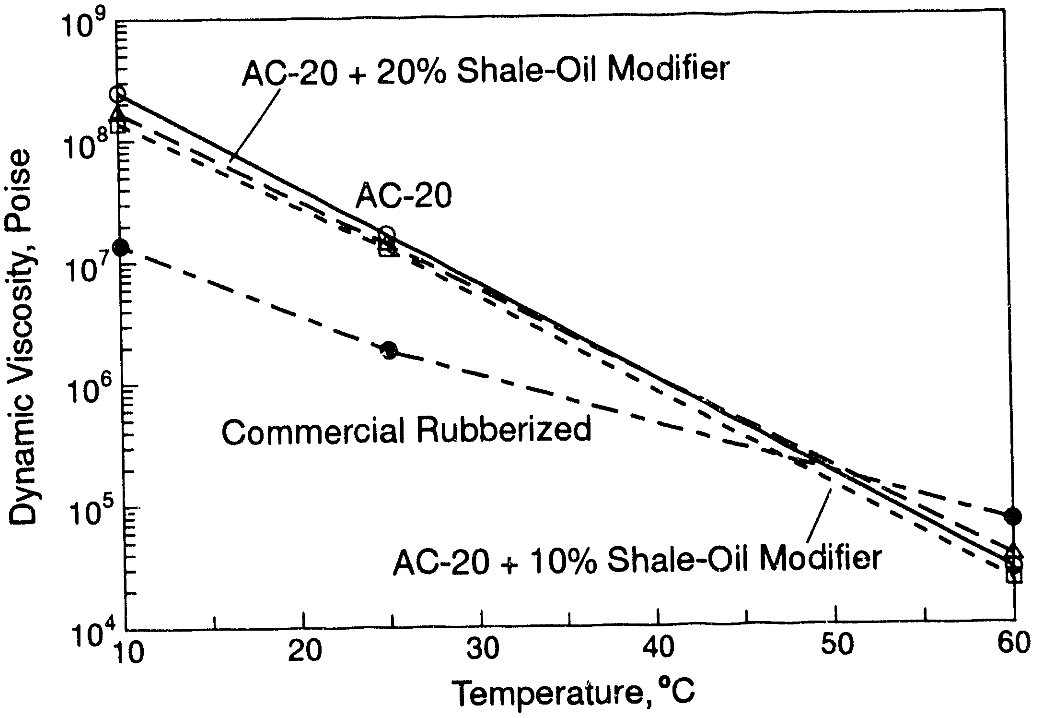

Figure 6. Dynamic Viscosity of Aged Samples versus Temperature

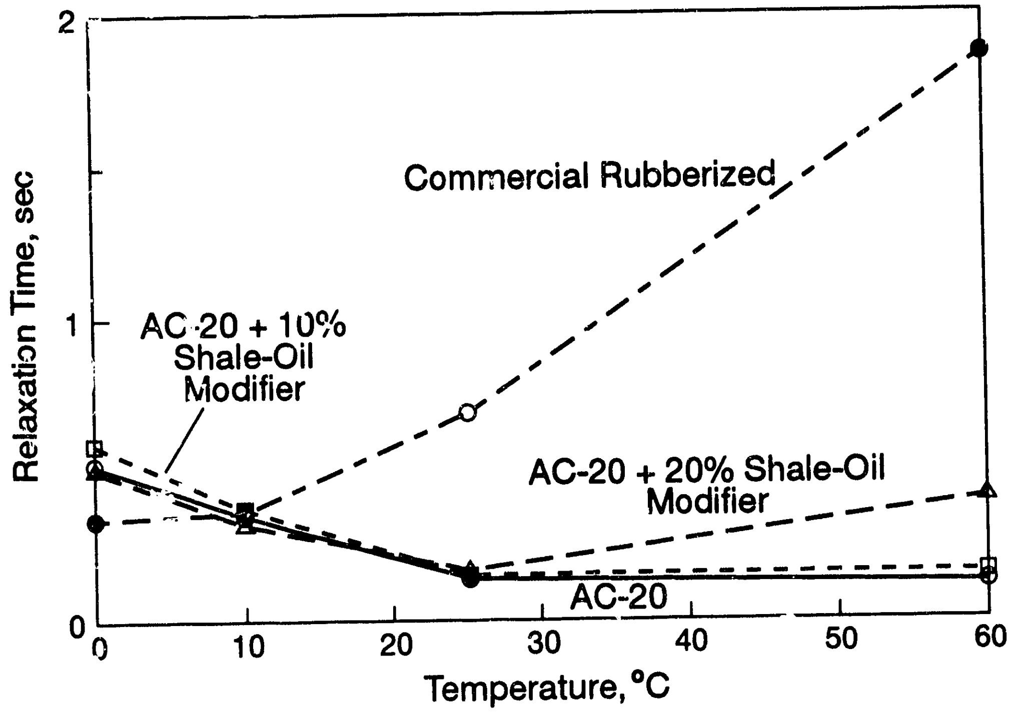

Figure 7. Relaxation Time of Unaged Samples versus Temperature

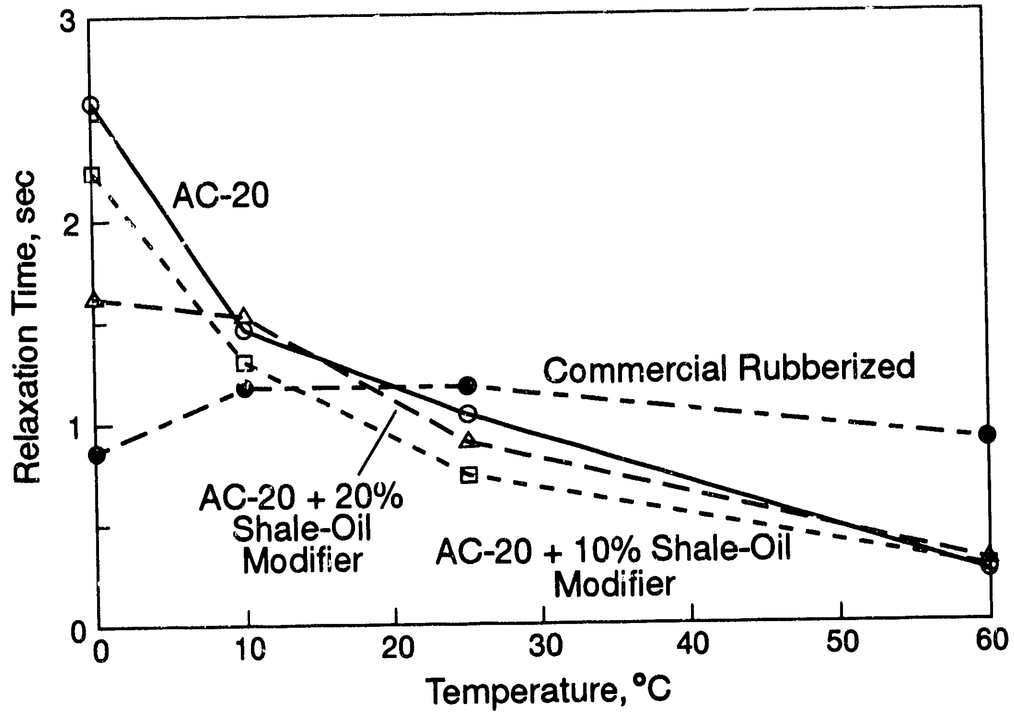

Figure 8. Relaxation Time of Aged Samples versus Temperature

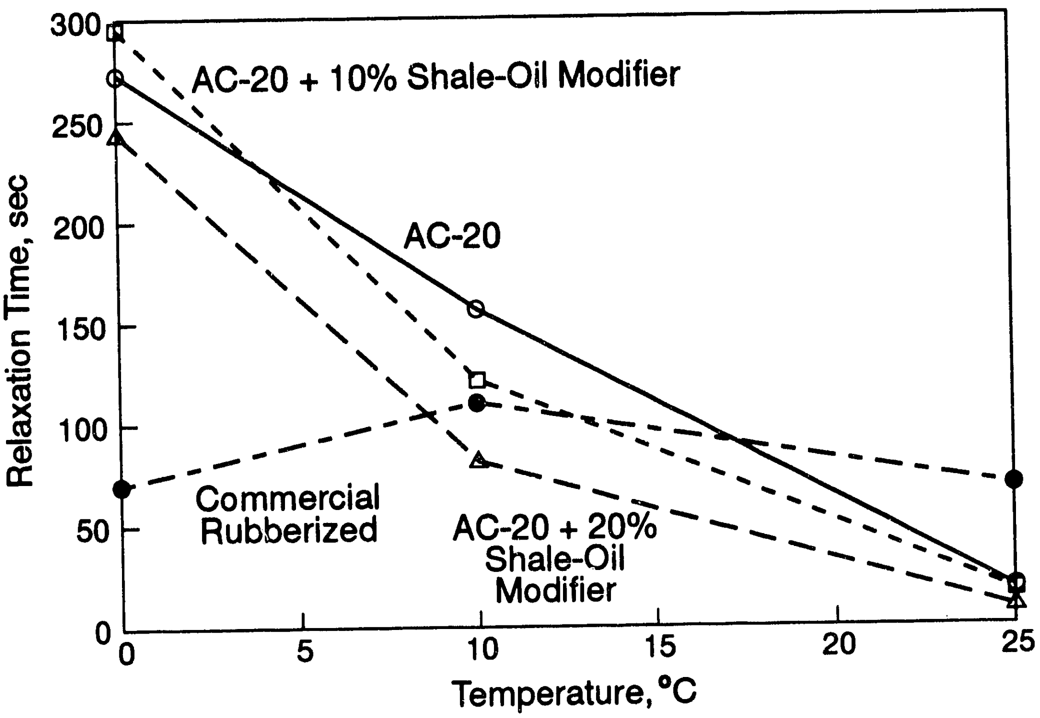

Figure 9. Relaxation Time of Briquets versus Temperature

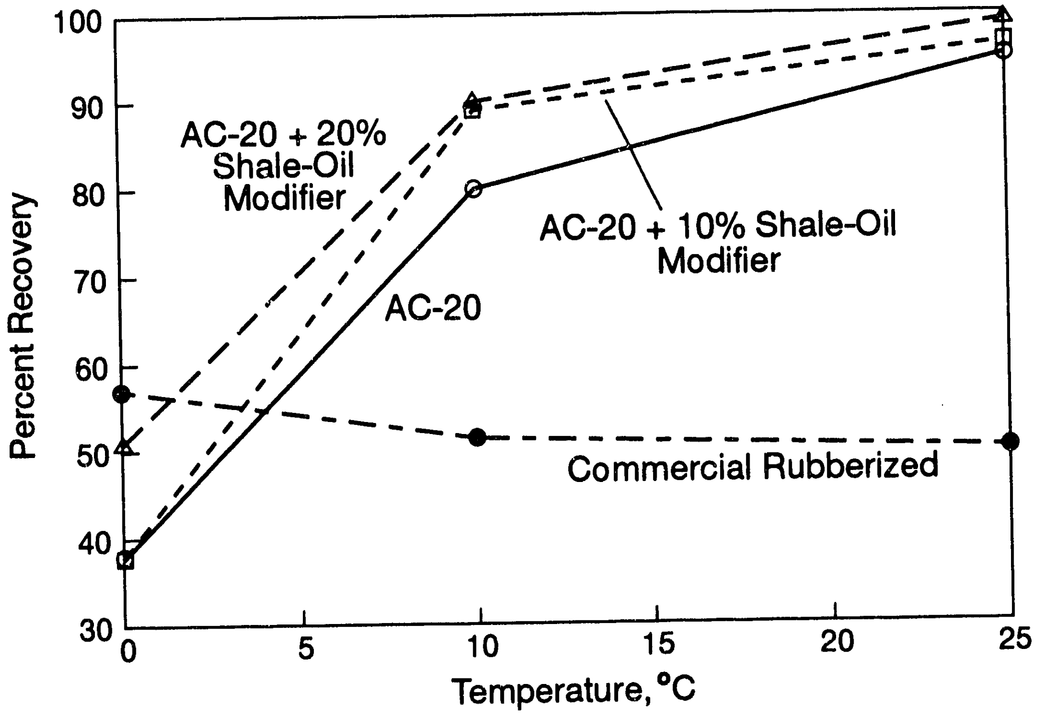

Figure 10. Percent Recovery of Briquets versus Temperature

DATE

FILMED

12 / 13 / 93

END