ASPHALT DURABILITY

S. C. Suhaka
Johns-Manville Sales Corporation

SUMMARY

Recent research has produced new test methods to detect changes in crude asphalt source and to rapidly predict weatherability. The methods were developed for coating grade asphalts intended for prepared roofing manufacture and do not apply directly to built-up roofing (mopping) asphalts in all cases. This work was sponsored by the Asphalt Roofing Manufacturers Association. Further work in determining compositional changes leading to failure is suggested.

I. INTRODUCTION

Asphalt durability is an area of roofing research which is receiving increased attention. Consumer demand for products offering the best value, frequent raw material changes resulting from crude shortages or scarcities and increased interest in petroleum chemistry as an outgrowth of the energy industry are just some of the reasons prompting this attention.

The Asphalt Roofing Manufacturer's Association (ARMA) has addressed the question of asphalt durability as part of their research program. Although intended primarily for prepared roofing, i.e. shingles and roll roofing, much of the information also relates to asphalts used in built-up roofing. The ARMA asphalt research program was undertaken in three phases. Phase I concentrated on the detection of changes in saturant or coating asphalt relating to changes in crude source or processing. The purpose of Phase II was the development of methods to allow rapid determination of asphalt weatherability. Phase III, in progress at this writing, is expected to lead to the development of a rational approach to upgrading substandard coating asphalts.

II. ASPHALT PROPERTIES — RELATIONSHIP TO PERFORMANCE

How does the asphalt used in a roofing system affect performance? Although many other factors are involved, the asphalt is a major determinent of the performance of prepared and built-up roofings. Asphalts from different crude sources can vary considerably in weatherability. Viscosity at service temperatures is a major property determining a specific asphalt's suitability for a given application. Rate of change of viscosity with temperature change is another important factor, for it determines the point at which asphalt loses plasticity and becomes vulnerable to brittle failure. Another factor in brittle failure is the rate at which stress is applied.

Asphalt's physical properties change as it ages. Weathering affects the rate of change in two general ways: through surface changes and internal changes.

One obvious surface change is oxidation initiated by ultraviolet light and/or heat. Mechanisms for this reaction have been proposed.[1,2] Surface hardening creates the "notch-effect" whereby a crack once started in the brittle surface can propagate into the softer layers below. "Alligatoring" is another surface related phenomenon wherein the asphalt layer forms this characteristic pattern due to surface tension and viscosity effects.

Internal changes also play an important role in asphalt weathering rate. Age hardening is observed even in asphalts kept in a cool dark environment. Part of this type of hardening is reversible upon reheating, but part is permanent.[3,4]

Exudation characterized by a surface concentration of the oily component is another internal change observed in asphalt. Other internal mechanisms also occur during weathering, such as loss of low molecular weight constituents and formation of water soluble materials at the surface.

III. COMPOSITION — RELATIONSHIP TO PHYSICAL PROPERTIES

Asphalt composition has been the subject of considerable investigation for over fifty years. Some work has been also done on the effect of composition on weatherability. Falzone[5] found that the average rate of change of total oils or dark oils or asphaltenes correlated well with accelerated durability. An excellent account of the relationship between chemical composition and the weathering of roofing asphalt was given by Corbett and Swarbrick.[6] Rather than consider the continuum of compounds from aliphatic to highly condensed, they developed a technique to look at fractions or families of generic compounds.

Additional work by Corbett[7] resulted in a separation of the following four fractions:

- saturated straight chain hydrocarbons termed saturates
- intermediate fraction designated napthene-aromatics, a mixture of cycloalkanes and moderately polar compounds
- a highly polar fraction called polar aromatics
- heptane insolubles or asphaltenes.

Corbett discusses changes in the relative amounts of the fractions due to blowing and weathering as well as reblending the fractions in varying proportions to study their effect on asphalt physical properties. Phase II of the ARMA program includes a method to predict asphalt weatherability based on the relative amounts of the four fractions initially present.

Initial composition of an asphalt depends on the crude source and the method of processing. Asphalt may be obtained:

- by straight run or vacuum distillation
- by solvent precipitation (usually with pentane or propane)
- by air blowing with or without catalyst
- as a thermal residue.

The softening point and penetration specification can be arrived at by more than one of these methods.

IV. RESULTS OF ARMA PROGRAM

In the mid 1970s, growing domestic crude scarcity and control of imported crudes by OPEC made quality control of roofing asphalt more difficult. In 1974 the ARMA Research Committee sponsored a contract for carrying out a research program in three phases.

Phase I required a practical and rapid test to determine whether change had occurred in the crude source. Such a change could mean that the quality of the asphalt has also changed.

A three-step procedure was developed. The first step involved observation of the color of the ash residue and comparison to a standard ash sample. A change in ash color could signal a process change, such as the addition of a catalyst. The second step was a determination of sulfur content. A change greater than 0.3 percent from the standard was considered to indicate a change in crude source. The third step if necessary involved comparison of the nickel and vanadium contents of the unknown asphalt to that of the standard.

The second and third steps were to be carried out only if doubt still existed as to whether there was a change in crude source.

In addition, relationships between the content of elements carbon, hydrogen and sulfur in asphalt were reported.[8]

Phase II has an objective the development of a practical test to predict the durability, and in particular the weatherability, of a coating asphalt.

The procedure was to be short enough to perform in one or two days. Two tests were developed, and they correlated well with the weatherability of fourteen asphalts determined by Weather-Ometer and outdoor exposures.

In the fractionation method of predicting asphalt durability (via the previously discussed Corbett procedure), a dispersion factor is calculated by dividing the sum of the polar aromatic and naphthene-aromatic fractions by the saturate fraction. A range of 1.4 to 5.3 was observed with the limits corresponding to the worst and best performing asphalts, respectively. The value of the dispersion factor corresponds well with overall durability ranking.

The second rapid method of determining durability, the asphaltene settling rate test, was anticipated by Kleinschmidt[9] when he observed a relationship between accelerated weatherability and rate of filtration of asphaltenes from the maltenes in solution. The settling rate test involves precipitation of the asphaltenes by heptane followed by observation of the rate of settling by means of a black light. A relationship was found between settling rate and weatherability as measured by outdoor exposure of asphalt films on aluminum panels.

Exactly why the test works is not fully understood, but the ability of the maltenes to keep the asphaltenes dispersed in solution appears to be a factor in maintaining a corresponding dispersion in the neat asphalt during service. A good discussion of asphaltene peptization, believed to relate to settling rate, was presented by Heithaus.[10] With some modification, the settling test has also been applied to paving asphalts.[11]

The two tests discussed, fractionation and settling rate, were developed specifically for coating grade asphalts used in prepared roofing. The application of these tests without modification to built-up roofing asphalts is not recommended. The lower weight percent of asphaltenes in the softer asphalt grade would have a direct effect on the dispersion factor and the rate of settling. Furthermore, durability rankings of the "standard asphalts" were based on samples in the 210-230°F softening point range and would not be expected to be the same for asphalts substantially outside this range.

Phase III was to yield a rational approach based on the use of additives, catalytic blowing, blending or some combination of these by which an unusable asphalt could be made usable. Four asphalts from Phase II were treated with 19 different additives at various concentrations. Increases in accelerated durability up to 200 percent and decreases up to 40 percent were observed. As expected, no single additive was found that was beneficial to all asphalts.

Still in progress are studies on the effect of catalytic blowing on durability, on the blending of saturant grade to overblown coating grade, and on the addition of additives prior to blowing.

V. FURTHER CONSIDERATIONS

A discussion of current asphalt research must include mention of high performance liquid chromatography (HPLC). Application of this technique to the study of petroleum-derived materials is expanding rapidly.[12]

HPLC allows the rapid separation and quantification compounds or classes of compounds from a mixture of many different molecular types. An asphalt fractionation procedure based on HPLC could be a reliable and rapid tool for determining the relative quantities of the functional types present. This information could be determined for many asphalts of known performance. Changes in composition from overheating or weathering could be determined and would give insight into the mechanisms leading to asphalt failure. Knowledge of failure mechanisms could suggest methods for their prevention.

REFERENCES

[1] Beitchman, B. D., ***Journal of Research of the NBS***, Vol. 64C, No. 1, Jan.-Mar. 1960.

[2] Mayo, F. R., ***Accounts of Chemical Research***, Vol. 1, No. 7, July 1968.

[3] Ensley, E. K., ***Journal Inst. Petrol***, 59, 279 (1973).

[4] Ensley, E. K., ***Journal of Colloid and Interface Science***, Vol. 53, No. 3, December 1975.

[5] Falzone, J. P., ***Relation of Rate of Component Changes in Asphalts to Accelerated Durability***, National Bureau of Standards Internal Report (unpublished) June 1958.

[6] Corbett, L. W. and Swarbrick, R. E., ***"Composition as Related to Manufacturing and Weathering of Roofing Asphalt"***, ASTM STP 347, 39 (1963).

[7] Corbett, L. W., ***Analytical Chemistry***, Vol. 41, No. 4, April 1969.

[8] Hoiberg, A. J., ***I&EC Product Research and Development***, Vol. 19, No. 3, September 1980

[9] Greenfeld, S. H., ***"Report on the Evaluation of 21 Coating-Grade Roofing Asphalts"***, National Bureau of Standards Internal Report (unpublished) (July 1956).

[10] Heithaus, J. J., ***"Measurement and Significance of Asphaltene Peptization,"*** Symposium on the Fundamental Nature of Asphalt. Presented before the Division of Petroleum Chemistry. American Chemical Society New York Meeting, September 1960.

[11] Plancher, H., Hoiberg, A. J., Suhaka, S. C., and Petersen, J. C., ***Proceedings Association of Asphalt Paving Technologists Technical Sessions***, Vol. 48, 1979.

[12] Altgelt, K. H., Gouw, T. H., editors, ***Chromatography in Petroleum Analysis***, Marcel Dekker Inc., New York 1979.