A STUDY OF TRANSLUCENT ASPHALTIC FILMS

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SYNOPSIS

Thin films of asphaltic materials have been weathered naturally and artificially and then studied microscopically by means of transmitted light One reaction, designated as coagulation, occurs in some positive Oliensis spot test materials under nearly all test conditions Observations and solubility characteristics indicate the coagulated film, at its formation time, to be composed of a dispersed solid phase and a continuous liquid phase This reaction is believed to be very important in that it gives a method of determining the compatibility of an asphalt mixture

Other characteristics such as hardening, checking, wrinkling, flocculation, precipitation, and the formation of waxy bodies have been observed microscopically Photomicrographs of these asphaltic film characteristics are presented

The determination of the quality and durability of bituminous materials is a perplexing problem of great economic importance

Low cost roads remain low in cost only so long as the elements of construction remain in serviceable condition While other elements enter, the bitumen remains a large factor in determining the success or failure of any bituminous construction

Lagging far behind the rapid development of the use of bituminous materials has been the development of accurate tests to determine the true quality and serviceability of these materials Many tests have been proposed to determine these factors, which are derived largely from the examination of successful materials through their physical characteristics The industry, of necessity, produces material to meet the conditions of test With changes of methods, the relationship between the test and quality and serviceability changes, and the determination of quality tends to return to its former indefinite status

This paper represents the work undertaken during the past two years to obtain a more satisfactory test for quality and durability of asphaltic materials A new method of attack has been used in a study of the reactions occurring in very thin translucent film of bitumen when exposed to agencies tending to decompose or alter the structure of the material

An examination of the character of decomposed material existing in bituminous mat surfaces in 1933 first directed attention to the possibilities of a microscopic investigation of asphaltic films A preliminary survey was begun in 1933 and was continued at intermittent intervals until a more complete investigation was started in the Road Materials Laboratory of the Kansas Highway Commission in June, 1936

Films of such thickness as to be translucent to light under the microscope permit a direct observation of the physical reactions taking place within the film This thinness permits acceleration of decomposition and alteration much greater than that obtainable in films of greater thickness

The reaction of translucent films has been studied under six conditions of exposure, classified as follows 325° F, 140° F, mild ultra-violet infra-red, cold quartz 140° F, natural weathering and by carbon dioxide and oxygen gases at 325° F The two tests designated by temperature were performed in darkness with the film in contact with air

The mild ultra-violet infra-red test was performed by use of a 250 watt

General Electric CX lamp. This lamp is a high temperature incandescent type with a special envelope. The characteristics as furnished by the manufacturer may be summarized as follows:

	Per cent
Ultra-violet, 3,500 to 4,000 A.U.........	0.15
Visible, 4,000 to 7,500 A.U..............	17.51
Infra-red, 7,500 to 26,000 A.U...........	82.34

The cold quartz ultra-violet lamp uses a combination of mercury vapor and rare gases to produce radiations essentially those of mercury. The lamp normally operates at a temperature of approximately 115° F. The radiation data supplied by the manufacturer for the distribution between 1849 and 4358 Angstrom units may be summarized as follows:

	Per cent
2,536 A.U.	77.97
2,967 to 3,128 A.U.....................	11.69
3,657 to 4,358 A.U.....................	8.57

METHOD OF PRODUCING THE FILMS

It was found by experiment that film thicknesses of approximately 0.001 in. gave the most satisfactory results. This film is obtained by the use of a gage constructed of stainless steel which is drawn across the face of the slide on which is a small portion of the material to be tested (Figure 1).

Fluxed and liquid asphaltic materials require no heating to produce the desired film. Penetration or non-liquid asphalts require heating of the slide, asphaltic material and gage to the lowest temperature at which the film can be formed.

Film thicknesses greater than 0.001 in. have poor light transmission and render definition of the reactions difficult. Thinner films do not always produce reactions with sufficient clearness.

METHODS OF TEST

Heat: The heat tests were performed in the dark in constant temperature ovens with the film in contact with air. The first tests were run at a temperature of 325° F. This temperature represented a degree often reached in some paving operations and it was believed to be the maximum that could be used under the conditions of test.

Tests run at this temperature presented, in some materials, the greatest acceleration, reactions becoming visible in periods as short as one-half hour. Those materials reacting at this temperature usually gave strong indications of the reactions in 5 hr. and were well developed or completed in 24 hr.

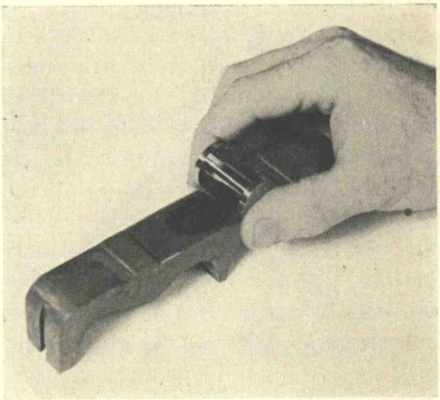


Figure 1. Gage for Forming Film

The second test was at 140° F. It was believed that this represented the maximum commonly reached by pavements in service, and that reactions presenting themselves at this temperature might be expected to give similar results in service with similar exposure.

The development of reactions at this temperature is slow in comparison with the time necessary at the 325° F. test. Tests at this temperature have been carried on over periods up to 2040 hr. Films presenting reactions in from two to five hours at 325° may require from 200 to more than 500 hours to present the reaction at the lower temperature. Materials have been found which present a reaction at one temperature and not at the other The reason for this is not definitely known

Infra-Red, Mild Ultra-Violet, 140° to 170° Test A General Electric CX Therapeutic lamp of 250 watt rating was used as a convenient method of obtaining mild ultra-violet radiations The large heat and visible radiation output of this lamp made temperature control difficult with the apparatus available It was not possible to hold the temperature at 140° as desired, but temperatures rose to 170°, which probably tended to accelerate reactions beyond that due to the ultra-violet radiations present

Cold-Quartz Ultra-Violet Test The fused quartz lamp, operating at approximately 115° F, uses as the radiation generating medium mercury vapor and a combination of gases which produce a strong radiation at 2536 Angstroms Initial tests run with this lamp at room temperatures of 70° to 90° F over a period of 60 days gave little distinctive reactions This lamp produces copious quantities of ozone In the initial experiment, the lamp was placed at a distance of 12 in from the specimens, with a cellophane shield placed 4 in above the tray The presence of large quantities of ozone above the shield may have effectively absorbed much of the ultra-violet present

A second investigation in which the specimens were placed 1½ in from the generating tube, fully exposed to the ozone present and maintained at a temperature of 140°, developed accelerated reactions in many materials, some of which presented no reactions at the other test conditions

Weathering Specimens were exposed to sunlight and outdoor air temperatures in a celluloid covered wooden box One group of specimens was run during the winter months, with a second series run during the summer months The temperatures in the box reached a maximum of 185° F, dropping to between 50° and 90° F during the night in summer exposure The winter exposures varied from about 70° to 10° F,

Gases and Heat Gas experiments were conducted at 325° F Oxygen and carbon dioxide were used, the gases entering one end of the sealed metal box and leaving at the other, controlled by a bubble flask on the outlet tube

The reactions as observed have been classified as follows A Clear, B Coagulated, C Flocculated, D Waxy bodies, E Checked, F Hardened The presence of scums, pits and wrinkling, when formed, has also been noted

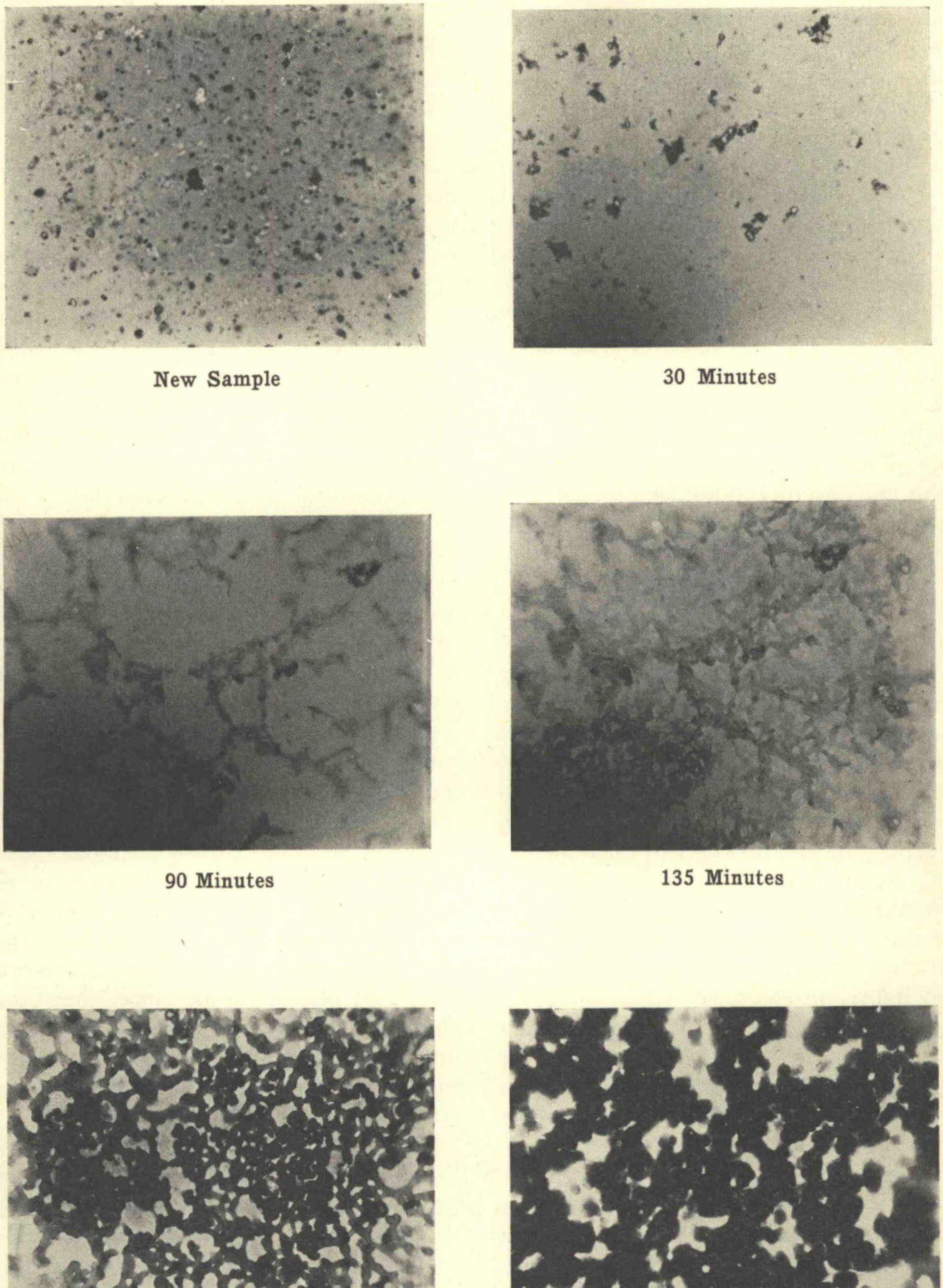
Of these reactions, coagulation is the most interesting in the forms in which it occurs, in the consistency with which it appears in certain types of material, and in the observations which have been made on its behavior This paper is therefore concerned largely with this reaction

Coagulation may be considered as the curdling or drawing together into nodular stringy form a part or the whole of the film The coagulation may consist of either a coagulated scum on the surface of the film, a single coarse structure, or it may be a lacy structure of great fineness composing the entire film

The formation of coagulation does not appear to be dependent on the presence or absence of the particles of carbon, sand, dirt or waxy bodies

OBSERVATION OF THE COAGULATIVE REACTION

Development of the Reaction at 325° F The development of coagulation in a positive Oliensis SC3 material is shown by progressive photomicrographs at 430X in Figure 2 The new specimen has a considerable quantity of suspended flocculent and carbonaceous material These materials have partially dissolved and partially coalesced at the end of 30



New Sample

30 Minutes

90 Minutes

135 Minutes

255 Minutes

12 Hours

Figure 2

min at 325° F The beginning of the coagulative reaction is also visible in the formation of numerous small light areas

Coagulation has begun to assume definite form at the end of 90 min of heating by the appearance of stringy dark matter At the end of 135 min this material has increased both in quantity and in size Portions of the coagulated material appear to form within the body of the film

A large portion of the film is in coagulated form at the end of 255 min The structure has become coarse A thin film of material remains on the surface of the slide This film is of a light yellow color and careful observation reveals that this film also presents a very fine coagulated structure

The reaction is complete at the end of 12 hr with the material in a very coarse, nearly opaque structure

Coagulation as a Separation Into Two Distinct Phases It is believed that coagulation is caused by a separation of the asphaltic material into two distinct phases One phase, that producing the actual stringy or lacy structure, appears to separate from the body of the material, and is of more consistency than the original or the remaining material The separation of this phase causes the remaining material to become more fluid and lighter in color

The second phase, the light yellow fluid, is not so evident in the tests run at high temperatures as it is in those run at lower temperatures and especially under the cold-quartz-140° test Coagulative specimens under the 325° temperature, if observed during the formation of the coagulation, will usually show clearly the separation of the solid phase The second phase appears to decrease after formation is in an advanced stage, appearing as a light colored layer of thin material on the surface of the slide Careful observation will usually show this material also to have assumed a coagulative form The decrease in the quantity of the liquid phase may be due partly to a change into coagulated material and partly to evaporation or to some other reaction at high temperature

Coagulative specimens at low temperatures (140° F) and natural weathering may show considerable separation into a solid and a liquid phase The presence of two phases is observable in the lacy or granular structure obtained in some coagulative materials under the cold-quartz-140° test as in Figure 3 Observing the grooving of the film under the microscope, the structure is evident throughout the film with the solid phase as a very fine, delicate material

When coagulated films of cutback asphalts are disturbed with a needle, the liquid phase quickly flows into the cracks, and more slowly into the groove produced by the needle The observations, made at room temperature, indicate a liquid phase of very low viscosity

Many coagulated films produced under a temperature of 140°, natural weathering or the quartz lamp exhibit a two phase system consisting of a continuous fluid phase and a discontinuous solid phase The solid phase appears to be composed of numerous small round or oval shapes which stick together and give the appearance of a lacy structure The fluid phase fills the interstices, but on prolonged exposure, tends to collect in an exceedingly thin layer between the surface of the slide and the film of granular coagulated material

Effect of Solvents on Coagulated Films The coagulative reaction during the development period is reversible by the addition of such solvents as CS_2, CCl_4, or benzol Both phases are soluble in these solvents during the development stages, but become insoluble or difficultly soluble after prolonged treatment The action of the solvent is to recombine the phases, or to dissolve the coagulated matter On evaporation of the solvent, the film is smooth and clear, with little or no evidence that the material had previously been in the coagulated state When subjected to the test conditions the film again develops coagulation

Effect of Gases The tests with various gases at 325° F are given in Table 1

It is evident that oxygen may cause a slight acceleration while CO_2 causes considerable negative acceleration, or possibly prevents coagulation, as in samples 96 and 97, when the formation is compared to air Some samples have been observed which have coagulated when heated, protected by a cover glass and therefore not in contact with air It appears that air and oxygen accelerate, but are not essential for coagulation of some materials This may be important in asphalt-aggregate structures where coagulation of the asphaltic material may occur without the presence of air

TABLE 1

Sample No	Oxygen—O_2		Carbon dioxide—CO_2			
	2 hours	4 hours	2 hours	4 hours	6 hours	11 hours
92	Clear	Clear	Clear	Clear	Clear	Clear
93	Clear	Clear	Clear	Clear	Clear	Clear
94	Clear	Clear	Clear	Clear	Clear	Clear
95	Clear	Clear	Clear	Clear	Clear	Clear
96	Coag	Coag	Clear	Clear	Clear	Clear
97	Coag	Coag	Clear	Clear	Clear	Clear
98	Coag	Coag	Clear	?	Coag	Coag
71	Clear	Clear	Clear	Clear	Clear	Clear
66	Clear	Clear	Clear	Clear	Clear	Clear
70	Clear	Clear	Clear	Clear	Clear	Clear
73	Coag	Coag	Clear	Clear	Clear	Coag
74	Clear	Clear	Clear	Clear	Clear	Clear

MATERIALS INVESTIGATED

The materials investigated may be classified as follows

Group 1 Seventeen samples, composed of RC, MC and SC type materials, produced at seven refineries and representing asphaltic material used in Kansas during 1936 for bituminous mat construction Both positive and negative Oliensis materials are represented

Group 2 Eleven samples of special material to investigate methods of manufacture and the effect on the reactions

Group 3 Fourteen samples, consisting of two series of tests made up of the originals and blends of the originals to produce both negative and positive Oliensis material

In addition to these groups, more than 150 samples of material, including original samples of asphaltic oils used since 1932 and 43 samples of asphalt extracted from existing pavements and mats, have been investigated by two or more of the methods given in this paper

Group 1

This group (Table 2) is composed of nine negative Oliensis and eight positive Oliensis spot test materials The Kansas specifications for positive Oliensis materials contained a special low-penetration ductility clause as follows the SC type of material and the distillation residues of the cutback type materials MC and RC shall be reduced to the designated penetration for that type by the method A S T M D243-28T The ductilities at the given penetration shall be 50 cm + at 77° F, 5 cm per minute The materials shall be reduced as follows

R C Cutback	40-50 penetration
M C Cutback	25-35 penetration
S C Asphaltic oil	15-25 penetration

Results All of the nine negative Oliensis materials remained clear at the end of the 325° and 140° heat tests With one exception, all of the negative material remained clear at the end of the CX, cold-quartz and natural weathering tests One sample, No 71, coagulated at the end of 142 hr under the CX lamp, at the end of 97 hr under the cold-quartz lamp and was coagulated at the end of 1176 hr of natural weathering

The positive Oliensis material presents more variation in behavior Five samples presented coagulation on all tests, three, Nos 65, 66 and 71, gave clear reactions at the end of the 325° test, two of these, Nos 65 and 71, gave clear reactions at the end of 2040 hr at 140° F No 65 also remained clear at the end of 1176 hr of natural weathering

It is therefore apparent that some positive material will show considerable resistance to coagulation It is interesting to note that the three positive Oliensis materials which show the greatest resistance to coagulation are of the SC type

Group 2

Samples Nos 77, 78, 79 and 80 are penetration asphalts produced from Venezuelan crude Two samples, 77 and 78, are negative Oliensis materials of 150 and 10 penetration respectively The others, 79 and 80, also of 150 and 10 penetration, are positive Olienses materials produced at a different refinery The difference in behavior of these materials with respect to either the Oliensis or the penetration test is not great The one difference is exhibited in sample No 80, the 10 penetration positive Oliensis material which had coagulated at the end of 1792 hr at 140° F

Samples 92 to 98 are asphaltic ma-

TABLE 2

GROUP 1

No	Type	Source	Spot	325°		140°		G E-C X 140°-170°		Cold quartz 140°		Weather	
				Clear	Coag	Clear	Coag	Clear	Coag	Clear	Coag	Clear	Coag
				Hours	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*
59	MC2	K-1	N	278		2,040		250		250		1,176	•
60	RC2	K-1	N	278		2,040		250		250		1,176	•
61	SC5	K-1	N	278		2,040		250		250		1,176	
62	MC2	K-2	P		18		528		67		17		192
63	RC2	K-2	P		18		528		84		17		192
64	SC3	K-2	P		18		528		67		17		192
65	SC3	T-1	P	278		2,040			250		17	1,176	
66	SC3	Mo-1	P	278			648		190		17		75
67	MC2	Mo-1	N	278		2,040		250		250		1,176	
68	MC2	T-2	N	278		2,040		250		250		1,176	
69	RC2	T-2	N	278		2,040		250		250		1,176	
70	SC3	O-1	P	278		2,040			310		35		27
71	SC5	T-2	N	278		2,040			142		97		1,176
72	MC2	K-3	P		18		528		67		17		192
73	RC2	K-3	P		2		528		48		17		24
74	MC2	K-3	N	278		2,040		482		149		1,176	
75	RC2	K-3	N	278		2,040		250		250		1,176	

terials produced by different processes. Samples 92, 93 and 94 are vacuum processed asphalts which have been progressively blown. No. 95 is a mixture of blown vacuum processed and blown fire-distilled materials. No. 96 is a cracked unblown asphalt; No. 97 is the same material blown. No. 98 is a mixture of a cracked and a blown fire-distilled asphalt. No. 92, the straight negative Oliensis material, resisted coagulation in all tests, as did also No. 93. No. 94, more highly blown than No. 93, showed less resistance and had coagulated at the end of 149 hr. under the cold-quartz-140° test. No. 95 indicated still more susceptibility to coagulation, and had coagulated at the end of 149 hr. under the cold-quartz-140° test and also at the end of 238 hr. under the CX lamp.

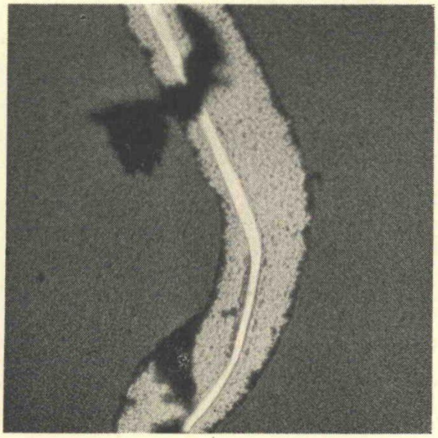


Figure 3. Lacy Coagulated Structure. 200 X

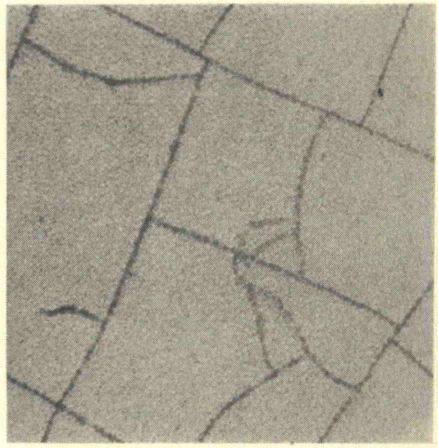


Figure 4. Coagulated Unblended Asphalt. 430 X

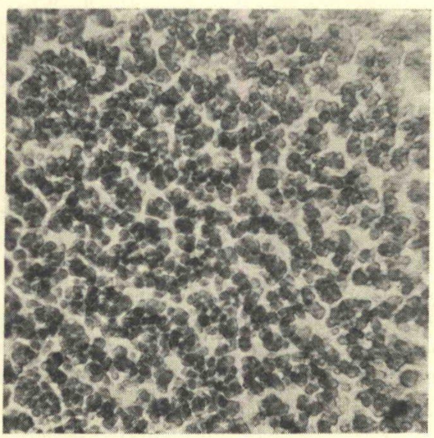


Figure 5. Coagulated Blended Asphalt. 430 X

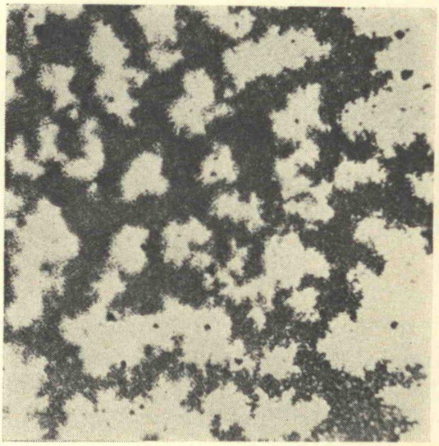


Figure 6. Flocculation and Coagulation. 430 X

Samples 96, 97 and 98 coagulated under all tests. The effect of blowing and blending is noted in the very rapid coagulation obtained in samples 97 and 98, where coagulation had taken place at the end of one-half hour at 325°. An acceleration may also be noted in the time required for coagulation under the CX lamp and weathering

Group 3

Results "A" Series This series presents coagulation beginning with sample A4, although the spot is still negative All samples containing more positive material than No A4 present coagulation at the end of the test

The condition noted in sample No 5B, which did not present the coagulative reaction at the end of 1052 hr at 140°, was checked by additional samples It appears that an equilibrium of blending occurred at this point It was noted that the spot from this sample appeared less positive than those immediately preceding, with smaller quantities of positive material in the blend It was first believed that an error had occurred in

TABLE 3
GROUP 2

No	Type	Source	Spot	325°		140°		G E -C X 140°–170°		Cold quartz 140°		Weather	
				Clear	Coag	Clear	Coag	Clear	Coag	Clear	Coag	Clear	Coag
				Hours	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*	*Hours*
77	150 Pen	Venz	N	118		1,792		482		149		268	
78	10 Pen	Venz	N	118		1,792		482		149		268	
79	150 Pen	Venz	P	118		1,792		482		149		268	
80	10 Pen	Venz	P	118			1,792	482		149		268	
92	Vac proc	Not blown	N	118		1,152		482		149		268	
93	Vac proc	Blown slightly	N	118		1,152		482		149		268	
94	Vac proc	Medium blown	N	118		1,152		482			149	268	
94+		Blown fire-distilled	P	118		1,152			238		149	268	
96	Cracked	Unblown	P		4		72		94		17		75
97	Cracked	Blown	P		½		72		46		17		24
98	Cracked +	Blown fire-distilled	P		½		72		46		17		24

"B" Series The "B" series tests were extended to include 1052 hr at 140° F The asphaltic materials are from a different source from those used in the series "A" tests In this series, series "B," two samples, 4 2B and 4 5B, presented coagulation at the end of 16 hr at 325° although the spot remained negative The 325° test was consistent, giving coagulative reactions on all samples after 4B

Coagulation did not develop in the 140° test until the spot had changed to positive in sample 4 7B The long exposure necessary to develop the reaction at this temperature is to be noted

the quantities involved, but additional samples of the same quantities corroborated the original results No coagulation resulted on this sample at the end of test, but a dark scum had formed on the surface

The results of this test make evident the differences in the behavior of materials when subjected to the two tests of 325° and 140° It will be noted that other materials have at times given differences in the other direction, being clear at the end of the 325° test and coagulated at the end of the 140° test

The effect of blending on the character of the coagulation is of interest as shown in Figures 4 and 5 Figure 4 is a photomicrograph of sample 9AB, the straight positive material Coagulation is of a fine grain and the material is of a light yellow color (32 hr at 325°)

Contrast Figure 4 with Figure 5, exposed the same period under the same wrinkling (Figure 10) The latter reaction often appears in films presenting no coagulative reaction, particularly under low temperature tests The wrinkling reaction is distinguished by the lack of any evidence of a separation into different constituents such as occurs in the

TABLE 4
DATA, SERIES A, GROUP 3

Specimen	Positive %	Negative %	Spot	325° 32 hours
A0	0 00	100 00	Neg	Clear
A2	9 00	91 00	Neg	Clear
A3	13 00	87 00	Neg	Clear
A4	16 00	84 00	Neg	Coag
A5	18 00	82 00	Pos	Coag
A5 5	19 00	81 00	Pos	Coag
A6	20 00	80 00	Pos	Coag
A6 5	21 50	78 50	Pos	Coag
A7	23 00	77 00	Pos	Coag
A8	26 00	74 00	Pos	Coag
A10	100 00	0 00	Pos	Coag

TABLE 5
DATA, SERIES B, GROUP 3

Specimen	Positive %	Negative %	Spot	325° 16 hours	325° 116 hours	140° 836 hours	140° 1,052 hours
1AB	0 00	100 00	Neg	Clear	Clear	Clear	Clear
1B	6 48	93 52	Neg	Clear	Clear	Clear	Clear
2B	9 00	91 00	Neg	Clear	Clear	Clear	Clear
3B	12 02	87 98	Neg	Clear	Clear	Clear	Clear
4B	15 00	85 00	Neg	Clear	Clear	Clear	Clear
4 2B	16 00	84 00	Neg	Coag	Coag	Clear	Clear
4 5B	17 00	83 00	Neg	Coag	Coag	Clear	Clear
4 7B	17 50	82 50	Pos	Coag	Coag	Clear	Coag
4 8B	17 75	82 25	Pos	Coag	Coag	Clear	Coag
5B	18 00	82 00	Pos	Coag	Coag	Clear	Scum
6B	20 05	79 95	Pos	Coag	Coag	Clear	Coag
7B	22 53	77 47	Pos	Coag	Coag	Clear	Coag
8B	25 00	75 00	Pos	Coag	Coag	Coag	Coag
9AB	100 00	0 00	Pos	Coag	Coag	Coag	Coag

conditions This material, sample 8B, has presented a much coarser coagulation than the original positive material This condition has been noted in other blended materials and points to such blending as one source of severe coagulative reactions

Wrinkling The coagulative reaction must be differentiated from that of coagulative reaction Wrinkling appears to be caused by the formation of a tough scum on the surface of the film, which, due to subsequent shrinkage of the material below the scum, develops a wrinkled appearance Films which are wrinkled, but show no evidence of coagulation, are designated as clear

Pits: Clear films may also contain numerous pits of the type shown in Figure 9. The cause of the pitting, which has been observed in several films, is not known. When this reaction is present, careful observation and an extension of the test is often necessary to determine whether the reaction is pitting, waxy bodies or the beginning of a coagulative reaction.

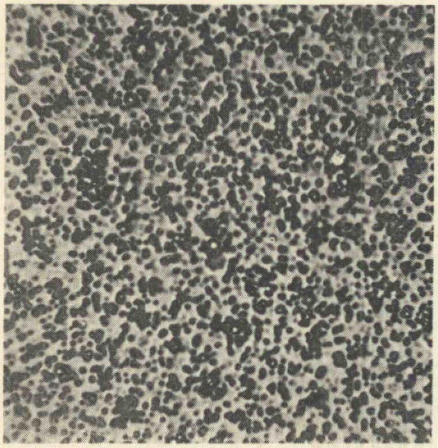


Figure 7. One Form of Coagulation. 430 X

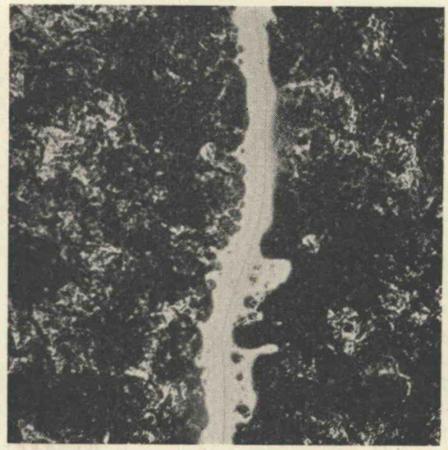


Figure 8. A Grooved Coagulation Film. 200 X

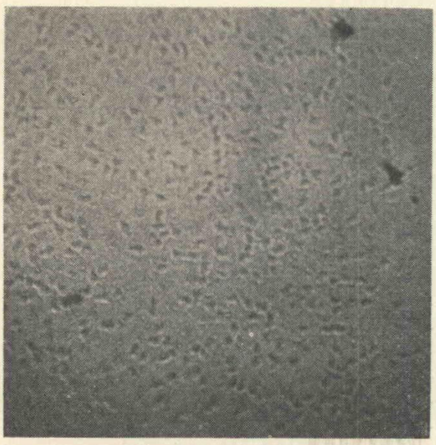


Figure 9. Clear Film with Pits. 200 X

Figure 10. Wrinkled Clear Film. 200 X

OTHER REACTIONS DESCRIBED

Flocculation: This material has been observed and photographed by other investigators, one of the latest by Lewis and Hillman,[1] the term "carbonaceous flecks" being applied. Due to the reversible solubility of this material, it appears that the material approaches an asphaltene in character.

The flock appears more commonly in positive Oliensis asphalts, particularly fluxed materials having high percentages of light distillates, such as the RC2. An increase in the amount of flock present has been noted in material of this type, RC2, which has been stored over a period

[1] *Public Roads,* Vol. 18, No. 5, July 1937.

of several months. When coagulation takes place in the presence of the flock, the flock is incorporated in the coagulative reaction. This is evident in Figure 6.

Waxy Bodies: This reaction was one of the first to be observed in the original is best observed under a cover glass, the crystals collecting on the under side of the glass in a fairly uniform layer. The crystals are optically active under polarized light, as shown in Figure 11, taken by this means.

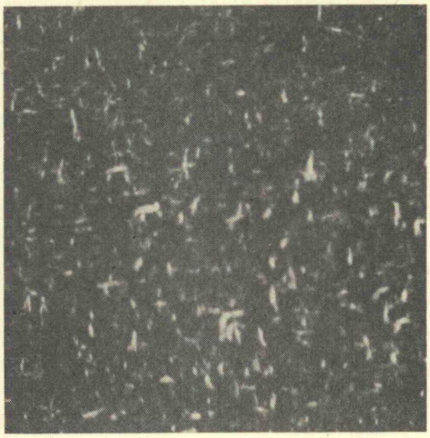
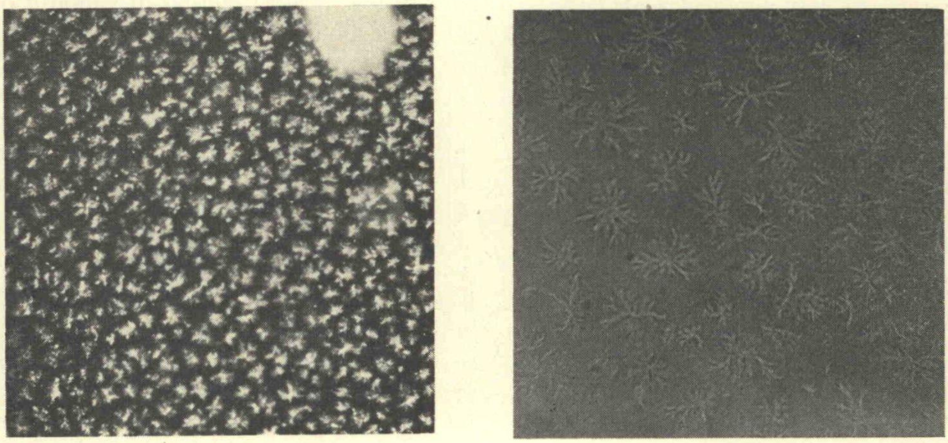


Figure 11. Wax by Polarized Light. 200 X

Figure 12. Wax Crystals. 200 X



200 X

430 X

Figure 13. Crystalline Wax Form at Two Magnifications

investigation. The appearance of this material is evidently due to the crystallization of the waxy material into various forms and sizes. The waxy material is apparently of less gravity than the surrounding asphaltic material and forms on the surface of the film. The reaction

Waxy material seems to be present in negative Oliensis materials to a greater extent than in positive Oliensis asphalts. Some negative Oliensis materials give considerable amounts of the crystals, as is evident in Figure 12. This material had a ductility of 100 cm. + on the penetration distillation residue. It is apparent that the presence of the material is not indicated to a large extent by the ductility of the material. It also appears possible that the amount of crystal precipitated is not closely related to the amount of waxy material present, but to the solubility of the waxy material in the asphaltic medium. Other forms of the waxy bodies after crystallization are shown in Figure 13.

The material may be crystallized out by heating to temperatures as low as 140° for a short period and then cooling to room temperatures. The crystals do not immediately appear on cooling, but will show halos or circles of lighter color than the surrounding film after from 10 to 20 min., and form crystals after perhaps 30 min. The formation is slow.

Checking. This reaction consists of the development of checks and cracks which usually extend through the thickness of the film. The reaction is not regarded as having any relationship to the coagulative reaction. Checking usually occurs as straight or smoothly curved lines which divide the film up into comparatively large geometrical figures. Checking may occur in either clear or coagulated films. Checking in a coagulated film is shown in Figure 4, checking in clear films is shown in Figure 14.

The most severe checking appears in naturally weathered specimens, particularly those exposed during winter months, where all the specimens developed severe checking. Temperature change and film brittleness appear to be the major factors causing checking.

Similar reactions have been used as a determination of failure by some investigators.[2] The importance of the reaction has not been determined in this investigation.

Hardening. As to the relative rates of hardening, a number of materials have been investigated by observing the condition of the film when grooved at room temperatures by a sharpened needle, the operation being performed under the microscope at 200 X. Several degrees of plasticity may be noted in the soft films, the consistency varying from sticky and adhesive to gummy and dead. The ultimate point of brittleness may be observed by the chipping and cracking of the film when grooved. The appearance of a plastic and a brittle film is shown in Figures 15 and 16 respectively.

SUMMARY

The study of translucent asphaltic films as presented in this paper is intended more as a survey of the reactions and the possibilities of the methods as a medium for further research, than as an intensive investigation into the factors involved.

It is believed that the coagulative reaction is a form of actual decomposition of the asphaltic structure, and as such, its observation has possibilities as an accelerated weathering test. The test also appears indicative of incompatible blends of asphaltic materials, and may be of assistance in securing more efficient blending operations in production.

Correlation with actual performance of coagulative susceptible and coagulative resistant materials, particularly with regard to the positive Oliensis materials, is not complete. It is known that some coagulative susceptible materials have given poor service in road construction, particularly in penetration type treatments.

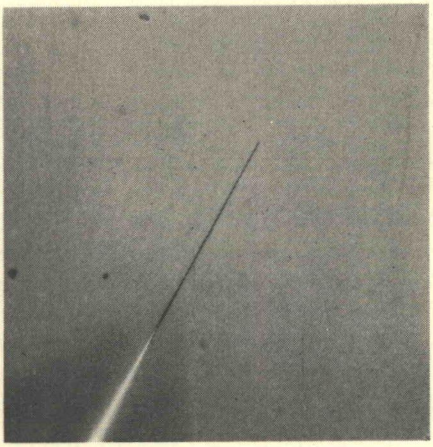
Tests performed on SC type positive Oliensis asphaltic materials extracted from bituminous mats which have given excellent service for periods of from six to seven years, have shown considerable resistance to the coagulative reaction. Materials extracted from two sheet asphalt pavements in service 20 and 26

[2] Strieter, *Proceedings*, A.S.T.M., July 1936.

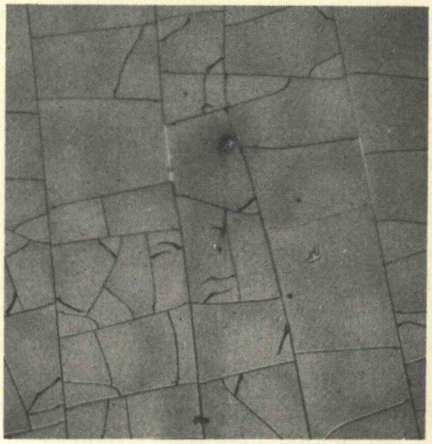
years, respectively, with excellent service records, were also highly resistant to coagulation.

Several materials of the SC positive Oliensis type in which both the original and extracted materials were highly susceptible to coagulation, have given fair service in dense crushed limestone bituminous mats for periods up to four years, with sealing operations performed during the last two years. More research is indicated to establish definite correlation between the reaction and actual serviceability.

The reaction of solvents in reversing the coagulative reaction may be important in the analysis of coagulative materials extracted from bituminous mats and pavements. The refluxing of the material by solvents may give an extracted material which would bear little relationship to the material existing in the aggregate-asphalt structure with the bitumen in a coagulated state.



430 X



200 X

Figure 14. Checking in Clear Films

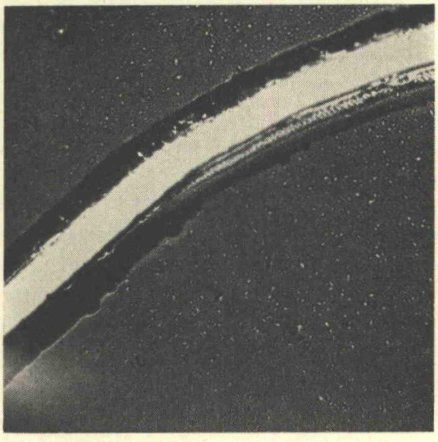


Figure 15. Plastic Film. 200 X

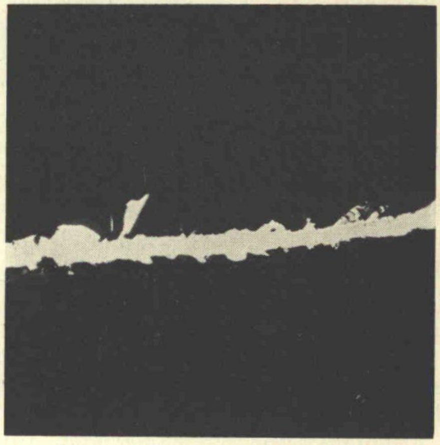


Figure 16. Brittle Film. 200 X

The separation of the asphalt material into two phases, one with a very low viscosity, increases the opportunity for preferential adsorption into certain aggregates such as limestone The material remaining as a binder would have few characteristics of the original material, and perhaps of the extracted material if the second phase were also extracted

The formation of the coagulative reaction in darkness and out of contact with air, at elevated temperatures, indicates the possibility of a similar reaction occurring in pavement structures with those materials

Flocculation of some materials appears to be due to solubility equilibriums The formation of the flocculent material may be either accelerated or reversed by the addition of carbon tetrachloride It has been noted that materials having appreciable quantities of flocculent matter usually are susceptible to coagulation

The effect of the presence of waxy bodies has not yet been determined Several materials which possessed good ductility character when subjected to regular laboratory tests, have been noted to have poor adhesive qualities when used in construction These materials, when investigated in translucent films, presented considerable quantities of waxy bodies Figure 12 is a photomicrograph of one of these materials

From theoretical considerations, the presence of this material appears objectionable The waxy material, being of less specific gravity (from 31° to 34° API)[3] than the asphaltic medium, tends to accumulate on a surface above the film From observations of this formation, it appears possible that actual displacement of asphaltic material may occur in favor of the waxy material The ultimate development of a waxy layer of material effecting more or less complete separation of the body and the asphaltic material is, from this view point, quite possible

This condition would result in a loss of bond between the constituents of an asphalt-aggregate structure with resultant failure, with the cause of failure not evident in any standard adhesive or ductility test The behavior of this material is being investigated

Checking of films is apparently accelerated by film brittleness and rapid temperature change Very brittle films often do not check if cooled slowly, but will check if cooled quickly The reaction might be used to indicate brittleness of the film under constant rate of cooling conditions The value of the reaction has not been determined in this investigation

The rate of hardening of the asphaltic material may be determined by observing the time required for reduction to a brittle film It is believed that this method may be of value in determining more accurately the true rate of hardening of asphaltic material when used in service, conditions approaching the test condition This condition is approached closely in asphaltic material used for sealing or surface treatments, where thin films are exposed to the action of the elements

There does not appear, at the present time, to be very much correlation between the rate of hardening as observed in the film investigation, and that secured from the material in service when incorporated in an asphalt-aggregate structure It has been noted that some extracted materials from pavements and bituminous surfaces which have given excellent service, and are still in excellent condition, have very high rates of hardening when in thin films at elevated temperatures It is evident that the aggregate structure is protective to a high degree, in the prevention of volatilization of the asphaltic material The very fine material present in some types of asphalt-aggregate structures, particularly with

[3] Nelson, W L, *Petroleum Refinery Engineer*, McGraw-Hill, p 581 (1936)

fluid or semi-fluid asphalts, appears to be of as much, or perhaps more importance in the protection of the asphaltic material than in the mechanical stability which this material gives to the completed structure

CONCLUSIONS ON THE COAGULATIVE REACTION

1 The coagulative reaction, as observed in some forms, is a separation of the asphaltic material into two phases, one tending towards hardness, the other towards liquefaction

2 The coagulative reaction may be produced in some materials by heat in darkness and out of contact with air

3 Coagulation may be produced by exposure to sunlight

4 Coagulation is accelerated by contact with air and oxygen and retarded by carbon dioxide

5 Coagulation is accelerated by exposure to ultra-violet radiations

6 Coagulation occurs more frequently in positive Oliensis materials than in negative

7 Some positive Oliensis materials have a high resistance to coagulation

8 Certain types of blending increase the tendency to coagulate

9 Coagulation may be produced at temperatures normally reached by pavements in service

10 The coagulative reaction is reversible at certain stages by the addition of solvents

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