Feb. 4, 1936. U. B. BRAY ET AL 2,029,290

ASPHALTS AND METHOD FOR PRODUCING SAME

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Fig. 1.

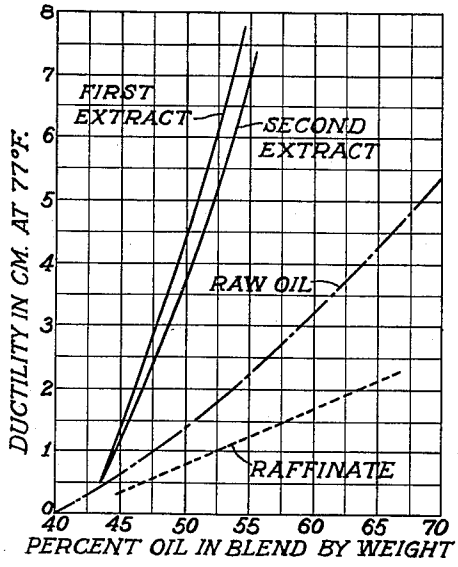


Fig. 2.

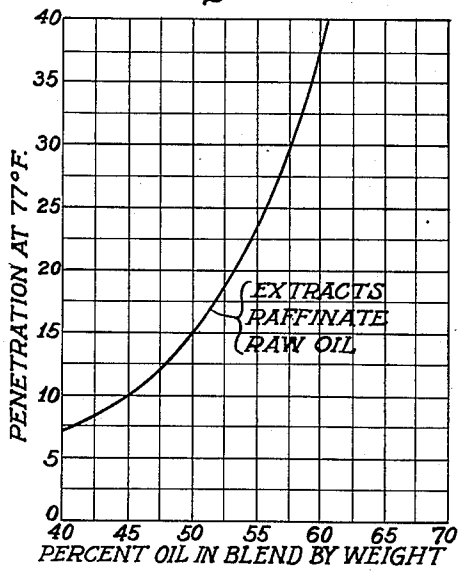


Fig. 3.

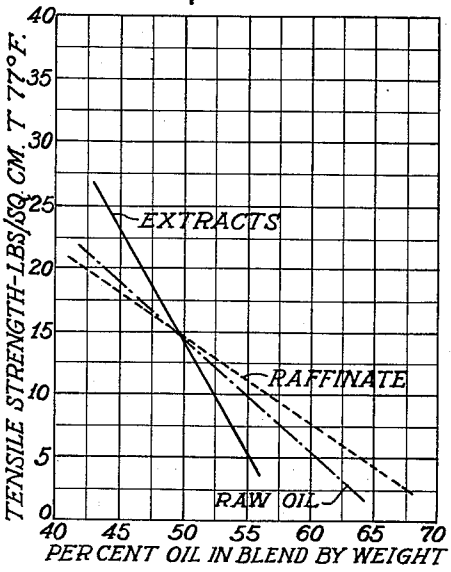
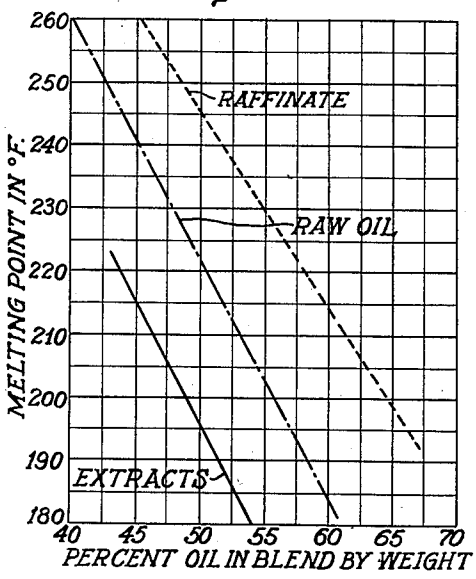


Fig. 4.



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ASPHALTS AND METHOD FOR PRODUCING SAME

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Fig. 5.

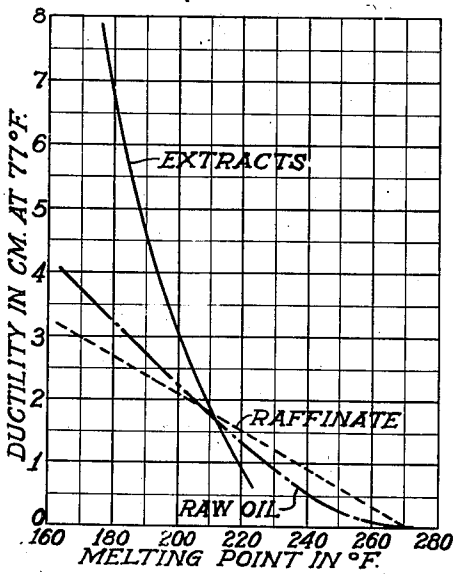


Fig. 6.

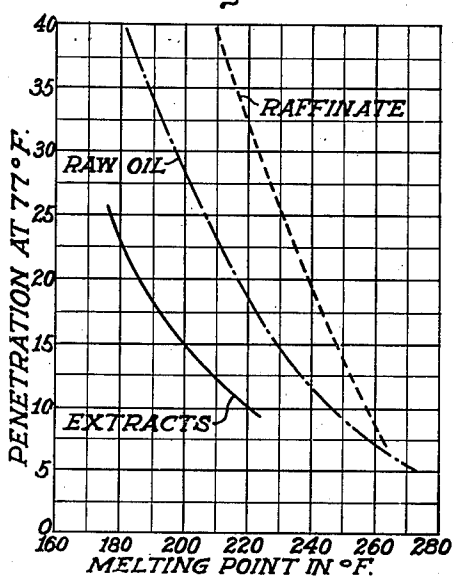


Fig. 7.

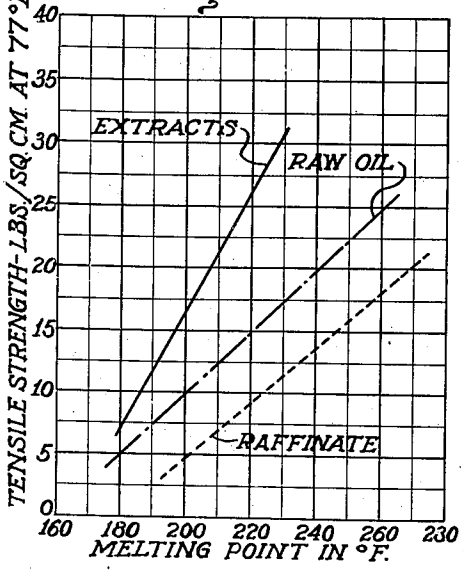
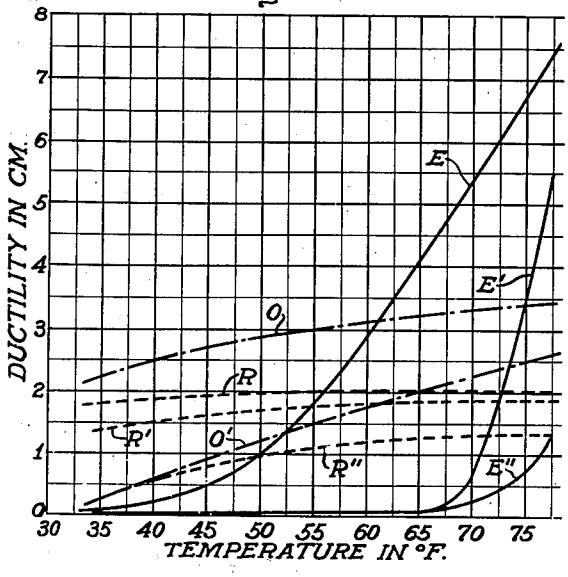


Fig. 8.



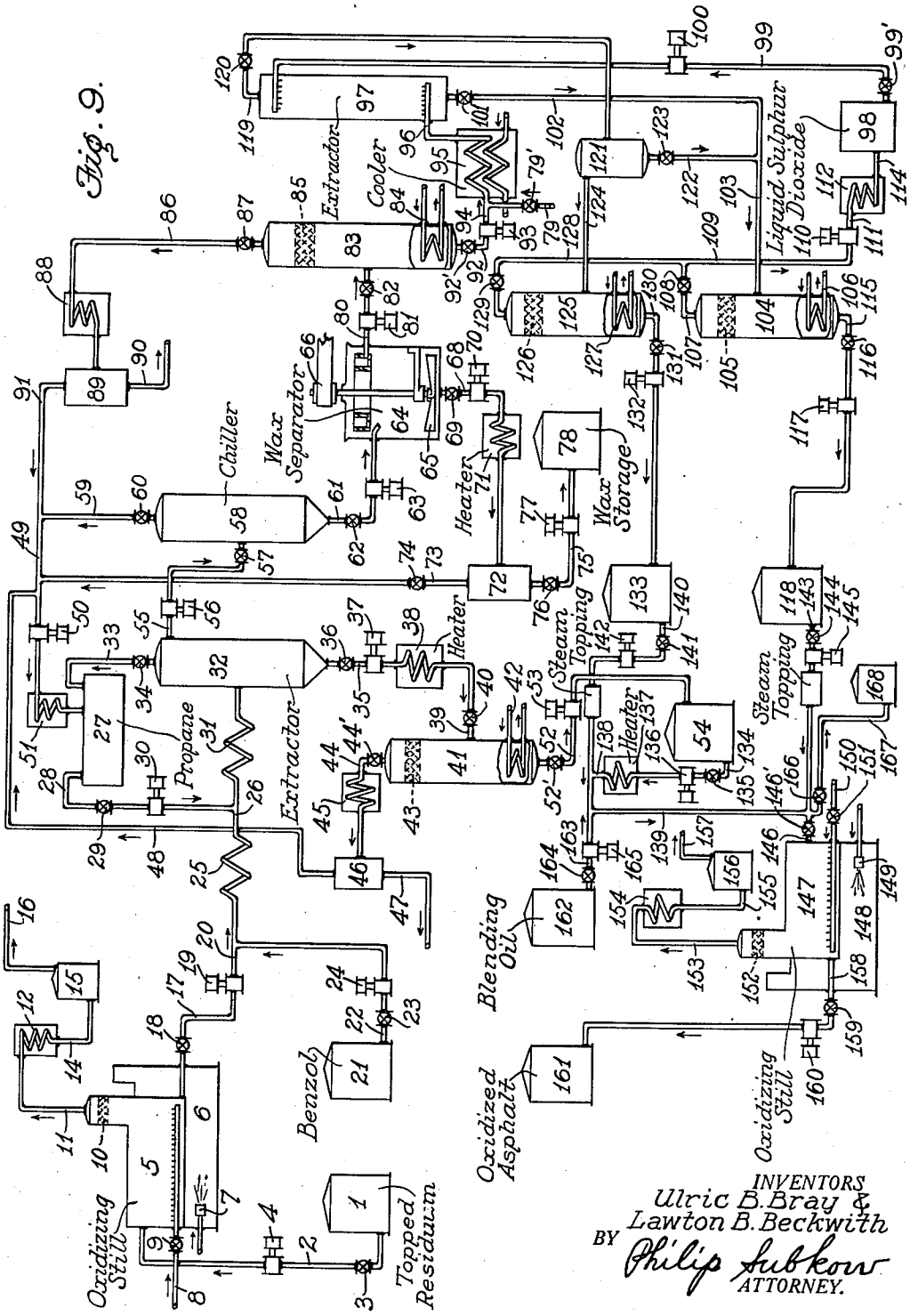
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Fig. 9.



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UNITED STATES PATENT OFFICE

2,029,290

ASPHALTS AND METHOD FOR PRODUCING SAME

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Original application August 7, 1933, Serial No. 684,094. Divided and this application December 18, 1934, Serial No. 758,072

15 Claims. (Cl. 196—74)

The present invention relates to asphalts and to methods for their production. The present invention is a division of our copending application Serial No. 684,094, filed August 7, 1933 now U. S. Patent 1,988,715.

It is well known that both steam refined and oxidized asphalt are composed of solid bitumens and oil. For the purpose of this discussion, the term "bitumen" will be used to designate the portion of the asphalt which is insoluble in liquid propane and the term "oil" or "raw oil" to designate that portion of the asphalt which is soluble in liquid propane. The amount of oil present in the asphalt is related to several physical characteristics of the asphalt such as the melting point and penetration. An asphalt having a low melting point usually contains considerable portions of oil, while one having a high melting point indicates the presence of a small amount of oil. The occurrence of large proportions of oil in high melting point air blown asphalt is not generally recognized but we have definitely established that such asphalt contains a considerable amount of oil and can be removed by extraction with solvents or by distillation with the aid of steam or under high vacuum.

We have discovered that if an air blown asphalt produced from a petroleum residue is separated as by means of solvents, for example, propane, or by distillation, into its oil and bitumen constituents and the bitumen constituent is blended with a selected fraction of the oil constituent and/or with other oils, asphalts may be produced having different characteristics from the original oxidized asphalt. Thus, if the oil constituent of the original asphalt is replaced in any desired proportion with more paraffinic fractions of the propane extracted oil or with other paraffinic or saturated type oils, the blended asphalt will exhibit a higher penetration at 77° F. for the same melting point and a relatively lower susceptibility to temperature change than the original oxidized asphalt. A blended asphalt of this type is more useful as a battery sealing compound or roofing cement than the oxidized asphalt from which it has been produced. On the other hand, if the oil constituent of the oxidized asphalt is replaced in any desired proportion with the more aromatic fractions of the extracted oil or with other aromatic type oils, the blended asphalt will have a lower penetration at 77° F. for the same melting point and a higher susceptibility to temperature change than the original oxidized asphalt. Such asphalts are suitable for saturating felt or fabrics because of their lower viscosities at the saturating temperature. They may also be employed in the manufacture of pipe line coatings and to replace the Gilsonite ordinarily employed in the manufacture of paints and storage battery boxes. The asphalts mentioned herein and forming the subject of our invention will be referred to as composite asphalts.

It is, therefore, an object of our invention to produce composite asphalt which is suitable for use as battery sealing compounds, roofing cements, for sealing cracks in pavement and for other uses where it is desirable that the asphalt have a higher penetration and ductility for a given melting point than an air blown asphalt of the same melting point and also a lower susceptibility to temperature change.

It is another object of our invention to produce synthesized asphalts which are suitable for saturating felts and fabrics where it is desirable that the asphalt have a higher susceptibility to temperature change. Other objects and advantages of our invention will be apparent from the following description of our invention taken from the drawings.

Figs. 1 to 8, inclusive, represent characteristics of the composite asphalt produced by our invention as compared with oxidized asphalt.

Fig. 9 is a schematic arrangement of apparatus for carrying out one embodiment of our invention.

Briefly, the asphalts forming the subject of our invention may be produced by first oxidizing a petroleum residuum or topped crude with air or other oxidizing gases to any desired melting point, for example, 200° F. The oxidation will reduce the penetration and ductility of the asphalt. The oxidized asphalt is then either steam distilled under high vacuum to remove approximately one-third of the asphalt as an overhead fraction as an oil, or it may be mixed with a solvent capable of dissolving the oil constituents of the asphalt and precipitate the bitumen. Solvents capable of effecting this are liquefied normally gaseous hydrocarbon solvents as ethane, propane, butane, iso-butane or mixtures thereof. Such hydrocarbon solvents are obtained by rectification of casinghead gasoline by the so-called stabilizing method now conventional in the natural gasoline industry. They comprise the overhead gaseous fractions of the stabilizing process. The gaseous fractions are liquefied by compression and cooling in the conventional manner and are drawn off into pressure chambers where they are maintained in the liquid state until they are used. A typical analysis of such a fraction is 6.72% ethane, 72.2%

propane, 19.91% iso-butane and 1.17% normal butane. The necessary pressure to maintain this fraction in a liquid state is approximately 125 lbs. per sq. in. gauge at 75° F. In the present discussion of this invention, this fraction or solvent will be referred to as "propane" or "liquid propane". It will be observed that other mixtures of these hydrocarbons may be employed, as, for example, we may employ a solvent having a greater proportion of ethane than that described above. For example, we may prefer to use a solvent comprising essentially 30% ethane and 70% propane.

When employing a liquefied normally gaseous hydrocarbon solvent to effect a separation of the oxidized asphalt into its oil and bitumen constituents, it is preferable to first cut the asphalt back, that is, reduce its viscosity, with a solvent which is liquid at normal temperatures and pressures. Such solvents may comprise naphtha, benzol and mineral spirits having a boiling range of 300° F. to 400° F. This will facilitate subsequent contact of the oil with the lighter solvent, i. e. propane.

The benzol solution having the consistency of a heavy road oil may then be extracted with approximately 300 to 500 volume percent of the liquid propane under pressure sufficient to maintain the propane liquid at atmospheric temperature. The propane phase of the extraction is then decanted and distilled to remove propane and benzol from the oil remaining as still bottoms. This oil may be further extracted with more propane to precipitate bitumen which has been carried over into the propane layer because of the presence of the benzol in the primary extraction. The bitumen phase from the primary extraction may be further washed with a fresh charge of propane to remove any unseparated oils from the first extraction. The washed bitumen is mixed with a small quantity of additional bitumen precipitated in the re-extraction of the oil. The oil recovered in the rewashing of the bitumen is mixed with the oil of the primary extraction. If the oil separated from the asphalt contains wax this may be separated by refrigeration and settling or filtration.

The oil is then separated by means of a selective solvent, such as liquid sulfur dioxide, into an oil having a low gravity viscosity constant, i. e. low temperature viscosity susceptibility and one having a high gravity viscosity constant, that is, a high temperature viscosity susceptibility. The oils having a low gravity viscosity constant are those resembling Eastern or paraffin base oils or saturated type oils, while oils of high gravity viscosity constants are those of the aromatic type. The gravity viscosity constant has been defined by Hill and Coates in the Journal of Ind. and Eng. Chem. in Vol. 20, page 641 of 1928. This constant represents the paraffinicity or naphthenicity of an oil. A high value represents a high degree of naphthenicity, while low values indicate relatively greater paraffinicity. Lubricating oils from natural crudes range from .903 for an extreme Gulf Coast type to .807 for an Eastern Pennsylvania type or even beyond. As solvents which will effect the separation of the oil into the two types, we have found liquid sulphur dioxide, mixtures of liquid sulphur dioxide and benzol, mixtures of acetone and benzol, chloraniline, nitrobenzene, furfurol, phenol, aniline or methyl formate useful.

Nitrobenzene or chloraniline alone, in addition to being an asphalt precipitant, also has, in some measure, the ability to split the oil in the above manner. Liquid sulphur dioxide has been found especially valuable as a solvent to separate the propane extract into oils having a low viscosity gravity constant, this oil being commonly known as the "raffinate" and an oil having high viscosity gravity constant which is known as the "extract". The raffinate may be further successively treated with fresh liquid sulphur dioxide to produce a second extract and also a third extract.

The characteristics of the oils thus extracted and the raffinate may be viewed from an inspection of Table 1.

TABLE 1

Extraction data from liquid sulphur dioxide treatment of raw oil separated from oxidized asphalt and physical and chemical tests on the raw oil

EXTRACTS AND RAFFINATE OILS

Oil	SO_2 treatment data		Physical tests			
	Vol. percent of SO_2 used	Percent by wt. of raw oil	Gravity °API	Viscosity Saybolt universal in secs. at 210° F.	Viscosity gravity constant	Analine point°C.
Raw oil	None	100	18.1	131.5	.876	75.5
First extract	0-300	20.3	11.5	191	.926	33.0
Second extract	300-600	8.7	12.8	170	.916	42.0
Third extract	600-900	5.8	14.2	146	.908	52.5
Final raffinate	900	65.2	20.7	129.5	.855	92.5

CHEMICAL TESTS

Oil	Ultimate analysis—percent by weight					Proximate analysis—percent by volume		
	S	C	H	N	Ash or O by diff.	Unsaturates	Aromatics	Other classes by difference from 100 percent
Raw oil	2.39	85.0	11.5	0.30	0.81	26.8	26.0	47.2
First extract	3.74	83.5	10.8	0.36	1.60	37.6	44.0	18.4
Second extract	3.54	85.6	10.6	0.38	−0.12	34.0	48.4	17.6
Third extract	3.15	83.5	11.4	0.33	1.62	26.0	38.0	36.0
Final raffinate	1.76	83.6	12.5	0.16	1.88	5.6	14.0	80.4

The extracts and final raffinate shown in the table were blended in various proportions with the bitumen separated by means of liquid propane from the oxidized asphalt. However, since the first and second extracts and final raffinate shows the greatest divergence in characteristics from the original oil, only these constituents were blended with the bitumen in various proportions.

Blends were not made with the third extract on account of the small yields of this material and less marked dissimilarity from the original oil. The blends of bitumen with the extract covered the range of 45% to 54% oil, while those of raffinate covered the range of 45% to 66% oil. The various tests on these blends are given in Figs. 1 to 8, inclusive. Figs. 1 to 4, inclusive, show the variation in ductility, penetration, tensile strength and melting point by the variation in amounts of the oils in the mixture. Figs. 5, 6 and 7 show the variation in penetration, ductility and tensile strength by variation of melting point of the various blends, while Fig. 8 is a plot showing the temperature susceptibility of ductility of the various blends. It will be observed that the blends of extracts and raffinate with bitumen are compared with a blend of the raw oil with the bitumen, the raw oil comprising the propane soluble portion of the original oxidized asphalt and from which the extracts and raffinate were produced. It may be stated that the blends of raw oil and bitumen correspond very closely in physical properties to ordinary air-blown asphalts of equal melting point produced by direct air blowing of the same residuum employed in the manufacture of the asphalt subjected to propane extraction.

It will be observed by reference to Fig. 1 that for any given percentage of oil, the blends of bitumen with sulphur dioxide soluble extracts have higher ductilities than blends with the raffinate, with the blends of raw oil falling in between. However, it will be noted from Fig. 3 that blending with the extract gives the lowest melting point and blending with the raffinate the highest for any given percentage of oil so that when blends of equal melting point are compared as in Fig. 5, it will be observed that the extracts give superior ductilities only for blends having a lower melting point e. g. 210° F. than the original asphalt. For melting points above that of the original asphalt, the blends of raffinate with bitumen are highest, while those with extracts are lowest in ductility for a given melting point.

Considering the susceptibility of ductility to change in temperature for asphalt of approximate equal melting points, it is seen from Fig. 8 that while blends of bitumen and sulphur dioxide extract are high in ductility at 77° F., they exhibit an exceedingly high rate of change in ductility with temperature so that the asphalts of this variety with a relatively high ductility at 77° F. show markedly less ductility at temperatures below 60° F. On the other hand, a blend with raffinate shows the lowest rate of change in ductility with temperature, while those with raw oil are intermediate as would be expected. It will be observed in Fig. 8 that curves O and O' represent the change in ductility of asphalts composed of raw oil and bitumen, the asphalts having melting points of 188° F. and 207° F., respectively. Curves E, E' and E'' represent mixtures of extract and bitumen, the mixtures having melting points of 182° F., 189° F., and 216° F., respectively. Curves R, R' and R'' represent mixtures of raffinate and bitumen, the mixtures having melting points of 196° F., 213° F., and 230° F., respectively. To the best of our knowledge, the low rates of change of ductility with temperature for the blends composed of raffinate and bitumen represent a marked improvement over naturally occurring asphalts or those produced by the usual methods. The advantages possessed by an asphalt which shows practically no change in ductility and lack of brittleness over the temperature range from approximately 30 to 80° F. are obvious.

Thus, for ductility at 77° F. higher values are obtained for a given melting point by blending the sulphur dioxide extract with bitumen until a melting point corresponding roughly to that of the original asphalt is reached, e. g. melting point of 210° F. For melting points higher than this temperature, e. g. 210° F., the higher values are obtained by blending the raffinate with the bitumen. To produce asphalt which will show the minimum of change in ductility with temperature, the best results are obtained by blending raffinate with bitumen. By solvent extracting the original asphalt, subjecting the thus separated oil to Edeleanu treatment, rejecting the extract portions and blending the raffinate with the bitumen, no appreciable change in ductility at 77° F. for the same melting point is obtained as compared to the original asphalt but the susceptibility of the ductility to temperature change is very greatly reduced. The asphalt in this manner will exhibit considerable ductility or lack of brittleness far below that temperature at which the original asphalt becomes sufficiently brittle to crack or chip quite easily.

By reference to Fig. 2, it will be observed that the penetration at 77° F. for the various blends of the different oils with the bitumen happens to be the same for the same percent of any of the oils in the blend so that the penetration at 77° F. is dependent only on the percentage of oil in the blend and not upon its treatment after propane extraction.

However, the melting point of the blend corresponding to a given percentage of oil is not independent of the nature of the oil but there is considerable variation in melting point for the same percentage of blends of extract, raw oil and raffinate. Thus, by referring to Fig. 6 and considering penetration for any given melting point, it is evident that the raffinate blends have the highest penetration and the extract blends the lowest with the raw oil blend falling in between. This is the equivalent of saying that for a given penetration the raffinate blends have the highest melting points and the extract blends the lowest melting points. When classified by the usual melting point and penetration relation, the blends of raffinate and bitumen show more air blown characteristics than the still run asphalts, while the extract blends tend to slow more steam blown characteristics.

While the theory involved in these phenomena is not established definitely, we believe that the reason for the peculiar behavior of the raffinate blends for a given melting point is that the state of dispersion of the bitumen in the raffinate blends is distinctly different from that in the extract blends, the raffinate being a relatively saturated and non-aromatic oil is not as good an asphalt solvent as the unsaturated and aromatic extracts. The result is that the raffinate

blends carry the asphalt in a dispersed or emulsified state as well as in true solution, while the extract blends are probably more homogeneous and more nearly approximate a true solution of asphalt in oil. This apparent two-phase structure of raffinate blends is probably influential in giving them a low susceptibility factor, while the low viscosity temperature susceptibility or low gravity viscosity constant of the raffinate oil itself is also probably a factor. In fact, the raffinate blends are thought to represent quantitatively an asphalt with exaggerated air blown characteristics.

Thus, it appears that for a given percentage of oil blended with the propane insoluble bitumen, the peneration of the blend at 77° F. happens to be independent of whether the oil taken is the extract, raw oil or raffinate. For a given melting point, however, the nature of the oil taken has a very marked influence upon the penetration at 77° F. because the melting point for a given percentage of oil varies markedly for raffinate, raw oil and extract. For a given melting point, the blends of bitumen with raffinate show the highest penetrations and the blends with extract the lowest with blends of raw oil and bitumen falling in between. For a given penetration at 77° F. corresponding to equal percentages of the different classes of oils, the melting points are different, the raffinate blends exhibiting the highest point and the extract blends the lowest. The higher penetration for a given melting point or a higher melting point for a given penetration for the raffinate blends as compared to the blends of extract and raw oil are believed to be due to the different states of dispersion of the bitumen in the raffinate. The physical tests of the raffinate blends represent exaggerated air blown characteristics and are thought to be due to the existence of two or more phases in air blown asphalt rather than one homogenous phase.

The tensile strength of asphalt is a property which is not usually determined but is, of course, of considerable importance in the selection of an asphalt for particular purposes, such as in the manufacture of sewer joint compounds and moulded plastics. The tensile strength of asphalt is measured by pulling apart in a suitable tensile strength testing machine and noting the force required to pull apart the ordinary ductility briquet of one square centimeter cross-sectional area at the narrowest point. Considering tensile strength as a function of percentage of oil in the blend, the variation in tensile strength between the blends of the different classes of oil may be viewed from an inspection of Fig. 3. However, these results may possibly be misleading because of the variation in melting point between the blends of the different classes of oil for a given percentage of oil. By inspecting Fig. 7 where the tensile strength has been plotted as a function of the melting point, it will be observed that the extract blends are highest in tensile strength and the raffinate blends are lowest in tensile strength with the raw oil blends falling in between. The lower tensile strength of the raffinate blends is thought to be due to the dispersed or two-phased nature of these blends as compared to the more homogenous extract blends. The raffinate blends are more rubbery in character than the extract blends and they have a slightly dull luster as compared to the bright luster of the extract blends. Thus, the extract blends are higher in tensile strength than the raffinate blends with the blends of raw oil and bitumen falling in between and this difference is believed to be due to the difference in state of dispersion of the blends.

From the above discussion of our invention, it is apparent that any desired type of asphalt may be produced by the proper combination of raffinate or extract with bitumen. However, it will be observed that this invention is not to be limited by recomposition of the raffinate or extract with the bitumen produced from the raw oil separated from the bitumen since raffinates and extracts of other oils or fractions of crude oil having other gravities, viscosities and viscosity gravity constants than those indicated in Table 1 may be substituted for those indicated above. Furthermore, other types of oils resembling the raffinate such as saturated type blending agents may be substituted for the raffinate. As examples of such oils, we may employ acid treated western oils, such as lubricating oils or solvent treated western oils or lubricating oils such as those produced by treatment with liquid sulphur dioxide, mid-continent or eastern oils of paraffin base or petrolatum. Likewise, the extract for blending with the bitumen may be substituted by other oils resembling the extract in composition. Such oils are the aromatic type blending agents. As examples of such oils, we may employ the liquid sulphur dioxide extracts from western oils or mid-continent or Pennsylvania lubricating oil stock or any kind of lubricating oil stock having a gravity of say lower than 15° A. P. I. Such oils having gravity of less than 15° A. P. I. are more aromatic than those above this gravity. We may also employ coal tar or coal tar distillates, cracked petroleum oils or residues or the polymers resulting from the Gray process, that is, the polymers resulting from treating cracked gasoline in the vapor phase with clay. The blends of oil with the bitumen may be further air blown to bring the blend to the desired specification as to melting point or other characteristics.

The above discussion has been made with great particularity with respect to the separation of oil from the bitumen by means of solvents. However, we do not wish to be limited to this exact procedure since the oil constituents of the oxidized asphalt may be separated by distillation under high vacuum and the oil recovered may be extracted to produce a raffinate and an extract in accordance with the above procedure and the separated constituents then recomposed with the bitumen in any desired proportion of the distillate may be discarded or employed as cracking stock and replaced by other type of oils mentioned above. As an example, we have produced a battery sealing compound by distilling approximately one-third of the oxidized asphalt and blending approximately 30 parts by weight of the bottoms to 70 parts of an acid treated heavy Western lubricating oil and further air blowing the composite asphalt.

It will be observed that for determining the melting or softening point, penetration, ductility and flash point, the following methods outlined by the American Society of Testing Materials were used:

Softening or melting point, Ball & Ring method	D-36-26
Penetration	D-5-25
Ductility	D-113-26T
Flash point, Cleveland open cup method	D-92-24

The blended or composite asphalt hereinabove described may be produced by the following method:

Referring to Fig. 9, a topped crude oil, such as fuel oil having a gravity of 14° A. P. I. and a viscosity of 100 seconds Furol at 122° F. is taken from tank 1 and passed into line 2 controlled by valve 3 and pumped by pump 4 into an oxidizing still 5 set in furnace 6 and heated by burners 7. The still is provided with perforated line 8 controlled by valve 9 for introduction of air into the still. The light hydrocarbons, fixed gases and excess air from the still 5 pass through mist extractor 10 and are removed from the still through line 11, condensed in condenser 12 and the condensate and uncondensed gases are then passed through line 14 into run-down tank 15. Fixed gases and excess air are vented through line 16.

The oxidation in still 15 of the fuel oil is carried on until a test of the asphalt shows the desired characteristics, as for example, a melting point of approximately 200° F., a penetration at 77° F. of approximately 15, a ductility of 2½ cm. at 77° F. and of 0 at 32° F. and a flash point of approximately 430° F.

Upon completion of the oxidation in still 5, the oxidized asphalt is withdrawn via line 17, controlled by valve 18 and pumped by means of pump 19 into line 20 where it is mixed with a liquid hydrocarbon solvent such as benzol taken from tank 21 and introduced into line 20 via line 22 controlled by valve 23 and pump 24. Approximately 35% by weight of the solvent is mixed with the asphalt for the purpose of cutting the asphalt back or reducing its viscosity and to thus facilitate contacting in the subsequent admixture with liquid propane. The asphalt and benzol is passed through turbulence coil 25 for the purpose of effecting intimate admixture of the solvent with the asphalt. The benzol solution of asphalt having the consistency of a heavy road oil is then passed into line 26 where it meets a stream of liquid propane taken from propane storage tank 27 via line 28 controlled by valve 29 and pump 30. Approximately three volumes of propane is mixed with one of the benzol-asphalt mixture. The propane may contain 30% ethane. The mixture is then passed through turbulence coil 31 for the purpose of effecting intimate admixture and then passed into the extractor or settling tank 32. In the extractor 32, a stratification of the mixture takes place into two layers, a lower layer consisting of bitumen and solvent and an upper layer of oil, benzol and propane. A pressure of approximately 125 lbs. per sq. in. gauge is maintained in tank 32 for the purpose of maintaining the propane in a liquid state during extraction. Equilibrium line 33 controlled by valve 34 connects the extractor with propane storage tank 27 also maintained at the aforesaid pressure. The bitumen phase settling to the bottom of tank 32 is withdrawn via line 35 controlled by valve 36 and passed to pump 37 which forces the bitumen through heating coil 38 where its temperature is raised to effect vaporization of entrained solvent.

The heated mixture is then passed via line 39 controlled by valve 40 into evaporator 41. Additional heat is supplied in evaporator 41 through closed steam coil 42. In evaporator 41, the vaporized solvent is passed through mist extractor 43 into line 44 controlled by valve 44' and thence through cooler 45 into separator 46. Condensed light oils and benzol are withdrawn via line 47 while the uncondensed propane passes via line 48 into line 49 to the suction of compressor 50 where its pressure is raised to that of the high pressure system, i. e. approximately 125 lbs. per sq. in. gauge, liquefied in cooler 51 and then passed into the propane storage tank 27. The bitumen is taken from the bottom of the evaporator 41 via line 52 controlled by valve 52' and pumped into tank 54 by pump 53. The supernatant solution of oil, propane and benzol is decanted from tank 32 and then passed to suitable apparatus for the separation of propane. The oil-benzol mixture is then subjected to refining with liquid sulphur dioxide hereinafter described.

However, if the original oil contained wax, it is preferable to remove this wax prior to the refining step. In this case, the supernatant solution of oil, benzol and propane is decanted from the extractor 32 and passed into line 55 by means of pump 56 which forces the mixture through valve 57 into chiller 58 maintained at a low pressure. In chilling column 58, sufficient propane vaporizes to reduce the temperature of the remaining material to a predetermined dewaxing temperature which causes the wax to precipitate from solution. The desired dewaxing temperature is obtained by controlling the pressure in column 58 by the proper operation of valve 60 on line 59 and compressor 50 which is connected to the evaporator by lines 59 and 49. The pressure to be maintained in column 58 will generally be about 0 lbs. gauge which corresponds to a temperature of approximately −40° F. As the propane solution passes through valve 57 its pressure is reduced so that a portion of the propane evaporates in the column 58 and the vapors pass out of the top through line 59 controlled by valves 60 then through line 49 to the suction of compressor 50 where the vapors are liquefied, cooled in 51 and passed to the propane storage tank 9.

The chilled oil dissolved in the propane and benzol carrying the precipitated wax is removed from the chilling column 58 through line 61 controlled by valve 62 by pump 63 which forces it into vapor-tight wax separator settler 64. In order to prevent ebullition or boiling in the wax separator during wax settling operation, pressure is imposed upon the solution of oil. This is accomplished by maintaining pressure within the separator by pump 63. As the chilled mass in separator 64 remains in a non-ebullient state, the wax settles out and is collected by vanes 65 operated by belt 66 connected to a suitable source of power not shown. The precipitated wax slurry containing propane settling at the bottom of the wax separator 64 is removed from the separator through line 68 controlled by valve 69 and pump 70 which forces the slurry through heating coil 71 where its temperature is raised to vaporize residual propane and is then passed into separator 72. Vaporized propane is passed to propane storage tank 27 via line 73 controlled by valve 74, compressor 50 and cooler 51. The propane-free wax is withdrawn from the separator via line 75 controlled by valve 76 and pump 77 into storage tank 78.

The chilled oil dissolved in propane and benzol and freed from wax is withdrawn from the vapor-tight separator 64 via line 80 by means of pump 81 which forces the mixture through valve 82 into evaporator 83. Heat is supplied for vaporizing the propane by closed steam coil 84. The vaporized propane passes through mist extractor 85 into line 86 controlled by valve 87, cooled in cooler 88 and is then passed into separator 89 in which any condensed naphtha and light oil which was vaporized together with the propane in the

evaporator 83 is withdrawn via line 90, while the vaporized propane passes into line 91 and then into line 49 to compressor 50, cooler 51 into propane storage tank 27.

The propane-free oil containing the heavier solvent, i. e. benzol, is removed from evaporator 83 via line 92 controlled by valve 92' and pumped by pump 93 into line 94 and passed through cooler 95 where the temperature of the mixture is lowered sufficiently, i. e. to approximately 10° F. for subsequent extraction with liquid sulphur dioxide. It is preferable to add further quantities of benzol to the oil so as to make the proportions of benzol to oil equal. The additional benzol may be introduced into line 94 by means of line 79 controlled by valve 79'. The cooled oil from cooler 95 passes by means of line 96 into the lower zone of extraction column 97. Liquid sulphur dioxide from storage tank 98 passes into line 99 controlled by valve 99' and pumped by pump 100 into the upper zone of extraction column 97. Due to the difference in the specific gravity of the oil introduced into the lower zone of the extraction column and the liquid sulphur dioxide introduced into the upper zone of the extraction column, these two liquids tend to separate. As the liquid sulphur dioxide passes down through the ascending column of oil, it dissolves certain components present. This solution of oil in the liquid sulphur dioxide is removed by means of line 102 controlled by valve 101 and line 103 and passed into evaporator 104 provided with mist extractor 105 where the sulphur dioxide present is vaporized with the aid of steam introduced through closed coil 106 and is removed by means of line 107 controlled by valve 108. The vaporized sulphur dioxide then passes via line 109 to compressor 110 where it is compressed and sent by means of line 111 to condenser 112 where it is liquefied and then by means of line 114 to sulphur dioxide storage tank 98. The sulphur dioxide free oil or extract containing benzol in evaporator 104 is removed through line 115 controlled by valve 116 and sent by means of pump 117 to storage tank 118.

The ascending column of oil in the extraction column 97 passes into line 119 controlled by valve 120 into auxiliary separator 121 where any remaining liquid sulphur dioxide is separated out and passes into line 122 controlled by valve 123 and line 103 into evaporator 104. The clear oil in the auxiliary separator 121 is removed through line 124 and is passed to evaporator 125 provided with mist extractor 126 where the sulphur dioxide present is vaporized with the aid of steam circulated through closed coil 127. The sulphur dioxide vapor is removed from the evaporator 125 by means of line 128 controlled by valve 129 and sent by means of line 109 to compressor 110 where it is compressed and passes by means of line 111 to condenser 112 where it is liquefied and thence through line 114 to the sulphur dioxide storage tank 98. The sulphur dioxide free oil or raffinate containing benzol in evaporator 125 is passed by means of line 130 controlled by valve 131 and is pumped by pump 132 into storage tank 133.

The foregoing discussion relative to the separation of the oil free from wax into an extract and raffinate by means of liquid sulphur dioxide has been described as being effected in the presence of the benzol which was originally introduced into the oxidized asphalt from storage tank 21. In other words, we have purposely retained the benzol in the oil in evaporator 83 and then added further quantities of benzol via line 79 so that the subsequent treatment with liquid sulphur dioxide may be facilitated. However, if desired, the benzol may be removed entirely from the dewaxed oil by means of the heat introduced in evaporator 83 and this solvent condensed and collected at the bottom of separator 89. The subsequent extraction of the oil may then be effected in the presence of equal volumes of other solvents, such as mineral spirits, boiling between 300 and 400° F. and introduced into the oil via line 79. It will be further observed that the raffinate or refined oil collecting in storage tank 133 and the extract collected in storage tank 118 will contain the heavier solvent. These oils may be steam topped at approximately 350° F. to remove the solvent prior to blending with the bitumen as will be hereinafter described. However, if desired, the admixture with the bitumen with either the raffinate or extract may be effected in the presence of the solvent and then the mixture steam-topped to remove the solvent prior to additional oxidation to be described.

In order to effect blending with the bitumen, the latter is withdrawn from tank 54 by means of line 134 controlled by valve 135 and pumped by pump 136 through heater 137 into lines 138 and 139 where it may be mixed with the raffinate from tank 133 introduced into line 139 via line 140 controlled by valve 141 and pump 142 or with the extract from tank 118 introduced into the bitumen by means of line 143 controlled by valve 144 and pump 145. Either mixture is then passed via line 146 into an auxiliary oxidizing still 147 set in furnace 148 and heated by burners 149. Air or other oxidizing gas is introduced into the still via perforated line 150 controlled by valve 151. Light oils, fixed gases and excess air are removed through mist extractor 152 and pass into line 153, thence through condenser 154, into line 155 and then into run-down tank 156. Fixed gases and air are vented through 157. The oxidation is carried on in still 147 until the admixture is brought to a proper specification whereupon it is removed from the still via line 158 controlled by valve 159 and pumped by pump 160 into storage tank 161.

The above description of the process has been made with reference to the blending of the bitumen with either the raffinate or extract produced from the original oxidized asphalt. If desired, and depending upon the amount of oil required in mixture to give a composite asphalt of desired specification as to melting point, penetration and ductility, additional quantities of the same blending oil may be introduced into the bitumen from storage tank 162 withdrawn via line 163 controlled by valve 164 and pumped by pump 165 into line 139. If desired, the blending oil from either tanks 118 or 133 may be supplemented or replaced by other oil of desired character maintained in tank 162.

The amount and character of the oil blended with the bitumen will depend upon the uses to which composite asphalt are to be put and upon the characteristics desired of the asphalt.

If desired, the blends of bitumen with raffinate, extract or extraneous oils may not be subjected to further oxidation as in still 147 and may be employed without any further treatment. By closing valve 146' and opening valve 166 on line 167 the blend may be passed to storage tank 168.

As an alternative method for producing a battery sealing compound or roofing cement, an oil

oxidized into asphalt to approximately 200° F. melting point, a penetration of 15 at 77° F. and a ductility of 2½ cm. at 77° F. and of 0 at 32° F. and having a flash point of approximately 430° F. may be distilled by steam distillation to remove approximately 30% of the oil and to leave hard bottoms of about 300° F. melting point. Approximately 30 parts by weight of the bottoms may be blended with approximately 70 parts of oil of the saturated type such as the raffinate produced by liquid sulphur dioxide extraction of the removed oil or of other oils or an acid treated Western heavy lubricating oil having a flash point of approximately 375 to 425° F. and a viscosity of 800 to 2000 seconds Saybolt universal at 100° F. or a high flash point lubricating oil produced from a mid-continent or Eastern crude of paraffin base or petrolatum. The blend of the bitumen or bottoms and the saturated type oil may then be blown additionally with air and steam to produce a synthesized asphalt having a melting point of 200° F., a penetration of 65 at 77° F., a ductility of 2½ cm. and 2 cm. respectively, at 77° F. and 32° F. and a flash point of 500° F. It will be observed that the penetration at 77° F. and the ductility at 32° F. have been increased considerably over the same tests on the original oxidized asphalt and the composite asphalt is more suitable as a battery sealing compound due to these increased properties than the original oxidized asphalt.

The foregoing exemplary description is merely illustrative of preferred modes of carrying out our invention and is not to be taken as limiting as many variations may be made within the scope of the following claims by a person skilled in the art without departing from the spirit thereof.

We claim:

1. A process for producing asphalt which comprises oxidizing an oil to produce an oxidized asphalt, separating said oxidized asphalt into an oil fraction and a bitumen fraction substantially free from oil and commingling said bitumen fraction with oil having a flash point between 375° F. and 425° F. and a viscosity of 800 to 2000 seconds Saybolt universal at 100° F.

2. A process for producing asphalt which comprises oxidizing an oil to produce an oxidized asphalt, separating said oxidized asphalt into an oil fraction and a bitumen fraction substantially free from oil and commingling said bitumen fraction with oil having a flash point approximately between 375° F. and 425° F.

3. A process for producing asphalt which comprises oxidizing an oil to produce an oxidizing asphalt, separating said oxidized asphalt into an oil fraction and a bitumen fraction substantially free from oil and commingling said bitumen fraction with oil of higher gravity viscosity constant than said separated oil.

4. A process for producing asphalt which comprise oxidizing an oil to produce an oxidized asphalt, separating said oxidized asphalt into its bitumen and oil constituents by means of solvents and blending said separated bitumen with oil having a higher gravity viscosity constant than the oil originally present in said oxidized asphalt.

5. A process for producing asphalt which comprises oxidizing an oil to produce an oxidized asphalt, separating said oxidized oil into an oil fraction and a bitumen fraction substantially free from oil by means of distillation and blending said separated bitumen with oil having a higher gravity viscosity constant than the oil originally present in said oxidized asphalt.

6. A process for producing asphalt which comprises oxidizing an oil to produce an oxidized asphalt, separating said oxidized asphalt into an oil fraction and a bitumen fraction substantially free from oil, blending said separated bitumen with oil having a flash point approximately between 375° F. and 425° F. and oxidizing said mixture.

7. A process for producing asphalt which comprises subjecting an asphaltic residue to oxidation with air to produce an oxidized asphalt, commingling said oxidized asphalt with a solvent capable of dissolving the oil constituent of said oxidized asphalt and to precipitate its bitumen constituent, separating the oil solvent solution from the bitumen, commingling said bitumen with an oil of higher gravity viscosity constant than the oil separated by said solvent and oxidizing said mixture.

8. A process for producing asphalt which comprises subjecting an asphaltic residual oil to oxidation with air to produce an oxidized asphalt, commingling said oxidized oil with a liquefied normally gaseous hydrocarbon solvent under pressure to separate said oxidized asphalt into its oil and bitumen constituents, commingling the oil constituent with a solvent capable of separating said oil into an oil having a low gravity viscosity constant and an oil having a high gravity viscosity constant, separating said oils from each other and commingling said oil having a high gravity viscosity constant with said bitumen and subjecting said mixture to further oxidation.

9. A process for producing asphalt which comprises subjecting an asphaltic residual oil to oxidation with air to produce an oxidized asphalt, separating said oxidized asphalt into its oil and bitumen constituents by means of solvents, commingling said oil constituent with liquid sulphur dioxide to separate said oil constituent into a raffinate and extract, commingling said extract with said bitumen and subjecting said mixture to further oxidation with air whereby an asphalt is produced having a lower penetration for the same melting point and a relatively higher susceptibility to temperature change than said first mentioned oxidized asphalt.

10. A process for producing asphalt which comprises subjecting an asphaltic residual oil to oxidation with air to produce an oxidized asphalt, separating said oxidized asphalt into its oil and bitumen constituents by means of liquid propane, separating said oil constituent into an oil having a low gravity viscosity constant and an oil having a high gravity viscosity constant, commingling said oil having a high gravity viscosity constant and said bitumen and adding to said mixture oils of higher gravity viscosity constant than the oil constituents separated from said oxidized asphalt.

11. A composite asphalt produced from an oxidized asphalt in which the oil constituent of the oxidized asphalt has been replaced with oil of lower paraffinicity, said synthesized asphalt having a lower penetration at 77° F. for the same melting point and a higher ductility at 77° F. for melting points below 210° F. than said oxidized asphalt.

12. A composite asphalt produced from an oxidized asphalt in which the oil constituent of the oxidized asphalt has been replaced with oil of lower paraffinicity, said synthesized asphalt having a higher ductility at 77° F. for melting points below 210° F. than said oxidized asphalt,

substantially the same penetration at 77° F. and a lower melting point than said oxidized asphalt for the same amount of oil in said asphalt.

13. A composite asphalt produced from an oxidized asphalt in which substantially all of the oil constituent of the oxidized asphalt has been replaced with oil having a flash point between approximately 375° and 425° F. and a viscosity of 800 to 2000 seconds Saybolt universal at 100° F.

14. A composite asphalt produced from an oxidized asphalt in which substantially all of the oil constituent of the oxidized asphalt has been replaced with an oil having a flash point between approximately 375° F. and 425° F.

15. A composite asphalt produced from an oxidized asphalt in which the oil constituent of the oxidized asphalt has been replaced with an oil having a flash point between approximately 375° F. and 425° F. said composite asphalt having a melting point of approximately 200° F., a penetration at 77° F. of approximately 65, a ductility of approximately 2½ and 2 cm. respectively at 77° F. and 32° F. and a flash point of approximately 500° F.

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