Influence of Waste Engine Oil Addition on the Properties of Natural Asphalt

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Abstract:
Disposal of waste engine oil (WEO) from vehicles is one of the significant problems that should be solved. One of the possible solutions to this problem is to recycle WEOs in effective way. Therefore, in the current research, the WEO from the maintenance workshops of vehicles (in particular cars’ type) were used as an additive material (filler) to enhance the physical and chemical properties of local natural asphalt from Heet city-Al Anbar governorate. Different weight ratios 0%, 2%, 4%, 6%, 8% were used to investigate their effect on the improvement of natural asphalt. To study the achieved improvement, the properties of natural asphalt before and after the addition have been studied by conducting physical and chemical measurements such as penetration, viscosity, degree of flicker, solubility, and ductility. The chemical tests are also conducted such as Infrared spectroscopy and ultraviolet spectroscopy. This study proved that it is possible to get rid of polluting wastes such as oil waste which are harmful to the environment and can be recycled as a useful material in improving the properties of natural asphalt to be used for flattening purposes according to Iraqi specifications (1196-88) of the first type and the international standards (ASTM D312 type A). The chemical composition of asphalt extracted from the springs before addition is very similar to the model in which the oil is added being hydrocarbons, which indicates that no chemical reaction occurred but rather a process of mixing the components through a spectral survey in the ultraviolet and infrared regions where the same beams appeared chemical bonds and transitions, with only different density.

1. Introduction:
The importance of this research is based on clearing the environment and tackling the problem of increasing quantities of used oils. In Iraq, there is no statistic of the amount of oils spilled in landfills, which may be spread in all cities of Iraq, especially since the number of oils consumed increases day after day without being able to deal with this problem and trying to take advantage of those large quantities dumped everywhere and that these oils have become a threat to the environment and people, which requires dealing with this issue with great importance commensurate with the risk it poses. Some people may have to dispose of used oils to pour them into the water, and this generates waste that has a direct or indirect impact on water, soil, and air. Water is one of the most polluted elements and therefore cannot be easily controlled. Asphalts and its products consist of decomposition of buried organisms for lack of oxygen. A mixture of many methane gas molecules with each other under certain conditions produces a compound that has new natural and chemical properties that differ from the original properties that formed from it, and this proves that asphalt and heavy hydrocarbons were formed in this way and can be formed as a result of the union of gases emitted from volcanoes in these areas in the ancient geological ages. There are some areas where oil spills lead to the formation of oil lakes and because of...
the evaporation of volatile substances quickly turn into oil pools. And asphalt is one of the oil
derivatives that remain on the face of the earth after the evaporation of light elements present in oil(3).
It is considered one of the wealth that Anbar governorate harnesses, which is filled with asphalt
springs, sulfur water, and natural gas.

1.1 Engine oil:
It is the oil used to lubricate the internal combustion engines. Its importance is to clean the
moving parts; prevent corrosion, improve its work, and cool the engine by removing heat from the
moving parts, and add other components to the engine oil so that it can withstand the high pressures.
Motor oil is derived from petroleum and non-petroleum chemicals, which are used in the petroleum
industries. The oil is generally composed of hydrocarbons and organic compounds consisting entirely
of carbon and hydrogen(4). There are two types of oil:

1.1.1 Monograde oil:
The degree of viscosity of the mono oil does not change with increasing or decreasing
temperature, and it is prepared from basic petroleum materials. This type of oil often used in old
engines or as tar oil.

1.1.2 Multigrade oil:
The viscosity level of the multigrade oil changes when the engine temperature changes and is
prepared from chemical and petroleum chemicals, and fine polymer particles. Compound oil (multi-
grade) is better than mono-grade oil, because it tolerates heat and pressure higher than mono, and it
also contains materials that are not in mono, such as insulating materials that reduce friction between
the cylinder and piston and chemicals that prevent rust formation(4).

1.2 Modulating the physical and chemical specifications of asphalt:

1.2.1 Modulating the physical specifications:
In this method, the asphalt is mixed with active substances such as calcium carbonate, calcium
hydroxide, Portland cement and other fillers(5,6) when adding sulfur to the asphalt In different
proportions that lead to adding different and required characteristics to the resulting material.
The results of the resulting asphalt are temporary and change after a short time and the reason is
the occurrence of the phase separation phenomenon of the asphalt and sulfur mixture(7).
Other methods of physical modification include the addition of various polymeric wastes, such
as polyethylene, polypropylene, natural rubber, and damaged tire rubber. Perhaps the most important
problem facing this type of modification is the non-melting of additives in whole or in part with the
asphalt, which gives a mixture of heterogeneous properties(8,9).

1.2.2 Modification of the chemical specifications:
The process of blowing asphalt with air with temperatures in the range of 180 °C occurs a
molecular oxidation process for components with high molecular weights and then increasing their
molecular weights, which leads to a change in asphalt specifications such as ductility, viscosity, and
plasticity(10). Methods aiming to bind the polymeric material to the hydrocarbon molecules of asphalt
by treating the asphalt with polymeric materials and this reaction is carried out using a catalytic block
reaction(11).

1.3 Previous studies:
Several studies were conducted on improving the natural asphalt where (Lee and et al(12))
studied the temperature affecting the chlorinated polyethylene mixture added as an improved material
for asphalt using granules of different sizes and noted that the addition leads to an increase in the
penetration factor and the viscosity penetration number when using flexible polymers Car tire crumbs
were used to improve the specification of tiling asphalt, and this study by (Mc. Gennis)(13) gave little
solidification and fracture asphalt.
The additive for asphalt is diverse, and the purpose is to give the durability of the asphalt to
resist wild (abrasion) or corrosion. Because of the movement of the tires and resistance to expansion in
summer and shrinkage in winter.
This study(14) proved that adding the polymer gives smoothness to the asphalt surface and there
is an improvement in the thermal properties of asphalt and increase the adhesion processes between
the components of the asphalt mixture. (Shatnawi) \cite{15} also confirmed that the rubber gives good physical properties.

For asphalt LDPE was used to improve the specifications of the asphalt, which gave an improvement in penetration by 70\%. The properties of the asphalt were greatly affected by the mixture between the polymer and the asphalt, the cause of which is the overlap between the asphalt and the polymer \cite{16}.

Different polymers could be used successfully and gave a bonded asphalt with its components at low temperatures, and this was confirmed by the study by (Kim and et al) \cite{17}.

In another study \cite{18}, LDPE was used to improve the asphalt of roads, as the polymer was mixed with two types (in the form of granules, and the form of a powder), so the percentage of addition of the polymer that gave the best engineering specifications for the asphalt is 4.5\%.

It was noted that there is an increase in the stability of asphalt, but there is also an increase in the gaps during the paving operations, and thus an asphalt breakage occurred.

The addition of copolymers with other thermoplastic polymers such as polyethylene and polypropylene gives improved asphalt with high stability even in very harsh environmental conditions \cite{19,20}.

In another study, the rubber tires used in the tire were added as a filling material that was added to the natural heat in different weight ratios, as a result of which the specifications of the natural asphalt were improved in a way that meets the Iraqi and international specifications as a moisture-proof flattening material \cite{19}.

A study by (Qadi and et al) \cite{22} came about predicting the dynamic behavior in the high temperature of the axle link as it used a common system of rubber polymer and a common polymer (homogeneous polymer - a common polymer) and this gave an output with good rheological properties.

To produce anti-pressure and high-stress asphalt (Zhou) \cite{23}, there are viscosity and elasticity factors that must be taken into consideration when mixing asphalt with other materials such as polymers and other fillers, as it was found that cracks of asphalt roads occur due to poor properties and bonding of these factors.

The study it was showed \cite{24} that it is possible to use natural bitumen after mixing with PVC in the form of waste by 30\% in the production of mixtures hot mix asphalt that can be used in the pavement layers instead of the asphalt bond produced from petroleum products for cold areas. PVC-modified natural asphalt has rheological properties similar to asphalt grades 58/100 and 70/100 according to local and international specifications which helps in reducing the cost of sidewalk layers.

The study aimed to achieve two goals:

First: the exploitation of natural asphalt and the expansion of its use fields by studying its properties and the possibility of improving them by adding inexpensive local materials found in the form of excreta, which are the waste oils used in car engines. Where the study meant to access properties of general significance to the validity of the asphalt material to suit application work.

Second: rid the environment of those wastes, which are constantly increasing in number, by recycling it as an environment-friendly project.

2 Experimental work:

2.1 Materials:

1. Natural asphalt from Al-Khader neighborhood, Heet city, Anbar, Iraq.
2. Industrial asphalt model produced in the Daura refinery, Baghdad, Iraq.
3. Used car engine oil (waste oil). WEO from the maintenance workshops of vehicles (in particular cars’ type)
4. Carbon tetrachloride CCl₄, 95\% purity, supplied by BDH.

2.2 procedures and analysis

2.2.1 Sampling:

Heet Natural Asphalt (HNA) is sprightly in weight, easy to flow, contains varying proportions of water and has an unacceptable odor due to the emission of gases such as H₂S. To get rid of
moisture, a certain weight of the model is taken in a glass container and placed in an electric oven for five hours at 160 °C. To measure weight loss by heating the model weight before making various measurements(25). The waste oil has been added as a filler to the natural asphalt in different weight ratios, 0%, 2%, 4%, 6%, 8%.

2.2.2 Physical measurements:
   a. Measurement of ductility:
      The measurement was performed according to the internationally approved (ASTM (D36-70)(26).
   b. Measurement of Penetration:
      The measurement was performed according to the internationally approved (ASTM (D5-83)(27).
   c. Measurement of solubility:
      Was measured according to the internationally approved method (ASTM (D2042-66)(28).
   d. Measurement of viscosity:
      The experiment was conducted according to the internationally approved (ASTM (D71-72a)(29).
   e. Measurement of flash point:
      Flash point was measured according to the internationally approved (ASTM (D92)(30).

2.2.3 Spectral measurements:
   1. Infrared spectroscopy: was measured following the procedure conducted in reference(31).
   2. Ultraviolet spectroscopy: was measured following the procedure conducted in reference(32).

3 Results and discussion
The results in Table 1 show that some physical properties (such as viscosity) decreased when the percentage of addition increased to (8%), while the permeability and ductility increased at the same percentage. Whereas, the solubility and the degree of flash showed a difference in the calculated values when compared with the Iraqi and international specifications.

The modification process shows a clear effect when compared to the standard specifications(33) as shown in table (1). As the penetration value is 121 °C higher than the value of the standard specification, that is, it hurts the results of asphalt. As for the degree of ductility, flash point, and solubility, it has degrees close to the standard specifications, that is, it lacks it slightly, and this shows that the results of the modification process were good. In terms of viscosity, the higher the temperature, the lower the degree of viscosity of the asphalt.

| Test                         | Iraqi Specification 88-1196 | ASTM Specification D312 | Waste oil-modified natural asphalt properties |
|------------------------------|-----------------------------|--------------------------|----------------------------------------------|
| Min.                         | Max.                        | Min.                     | Max. | % 2 | % 4 | % 6 | % 8 | Average |
| Penetration at 25°C          | 40                          | 50                       | 18   | 60  |     |     |     | 181.5   |
| Softening point °C           | 49                          | 58                       | 57   | 66  |     |     |     | 44      |
| Flash Point °C               | 246                         | 260                      | 230  | 205 | 215 | 239 | 238 | 225.4   |

Table (1) A comparison between the Iraqi and ASTM specifications for the results of modified natural asphalt(33).
3.1 UV spectrum analysis:

The following transitions in the UV spectrum can be distinguished for all models before and after the addition where the results are almost similar to the difference in absorption intensity:

- Excitation of the type $\pi-\pi^*$ at the location 407 nm as the excitation of the type $\pi-\pi^*$ appeared at the location of 275 nm of the model before adding (0%) as shown in figure 1, as well as a stimulation of the type $\pi-\pi^*$ at the site 281 nm for the model after adding (2%) as in figure 2, as a stimulation of the type $\pi-\pi^*$ appeared at the location is 269 nm for the model with the addition rate (4%), as in figure 3. Also, excitation of the type $\pi-\pi^*$ appeared at the location of 300 nm for the model with the rate (6%) shown in figure 4. Excitation of the type $\pi-\pi^*$ appeared at the site 375 nm of the model after adding (8%), as in figure 5, as well as a stimulation of the type $\pi-\pi^*$ at the 385 nm of the industrial asphalt model produced in the Daura refinery as shown in this figure 6.

| Viscosity at 135°C | 1220 | 512.5 | 437.1 | 337.5 | 350 | 250 | 377.4 |
|---------------------|------|-------|-------|-------|-----|-----|-------|
| Solubility in CCl₄ | 99   | 99    | 35    | 82    | 59  | 73  | 66    | 63    |

**Figure (1)** UV absorption spectrum for natural asphalt

**Figure (2)** UV absorption spectrum for modified asphalt at 2% waste oil
Figure (3) UV absorption spectrum for modified asphalt at 4% waste oil

Figure (4) UV absorption spectrum for modified asphalt at 6% waste oil

Figure (5) UV absorption spectrum for modified asphalt at 8% waste oil
3.2 FTIR spectrum analysis:

The results of the FTIR spectrometry of the confined area showed between 4000-400 cm⁻¹ that the effective groups present in the main components of the natural asphalt model and the industrial model of the Doura refinery that the absorption packages are similar and this indicates that the groups of the constituent components of the compounds are identical in terms of chemical composition and the type of bonds. We infer the presence of the C-H aliphatic atomizer at the range 2987-2986 cm⁻¹, as well as the presence of the C=C aromatic at the range (1518.10-1411.61) cm⁻¹ and the appearance of the C=O prosthesis of the carbonyl group at the range (1756.27) cm⁻¹. As well as the emergence of the aliphatic C-H at the range (1051.65-1051.44) cm⁻¹ and at the range (627.22-627.16) cm⁻¹ and the presence of the C-H aromatic as well as the appearance of the C-Cl bundle at the range (759.52-759.87) cm⁻¹ as in figure (7). When adding the used engine oil at a rate of (2%), we find a slight displacement and the chemical composition has not changed, but only a physical mixture has occurred, and evidence of the presence of an aliphatic C-H type at the range (2982.22) cm⁻¹ as well as the presence of a C=C aromatic at the range (1519.75) cm⁻¹ and the emergence of C=O for the carbonyl group at the range (1756.13) cm⁻¹ as well as the emergence of the aliphatic C-H type bend at the range (1051.40) cm⁻¹ and the range (626.95) cm⁻¹ and the presence of the C-H type aromatic and the appearance of a C-Cl bundle at the range (781.52) cm⁻¹ as shown in figure 8. As for adding the consumed engine oil by (4%), a slight displacement occurred and the chemical composition did not change, but a physical change occurred only and evidence of the presence of an aliphatic C-H type at the range (2984.91) cm⁻¹, as well as the presence of a type C=C uremic at the extent (1519.09) cm⁻¹ and the emergence of C=O for the carbonyl group at the range (1756.13) cm⁻¹ as well as the emergence of the aliphatic C-H type bend at the range (1051.21) cm⁻¹ and at the range (627.26) cm⁻¹ and the presence of C-H type aromatic and the appearance of a C-Cl package at the range (781.77) cm⁻¹ as shown in figure 9. When adding the engine oil consumed to the model at a rate of (6%), a slight displacement occurred and the chemical composition did not change, but a physical change occurred only with a change in the intensity of absorption and evidence of the presence of an aliphatic C-H type at the range (3013.19) cm⁻¹ as well as the presence of a type C=C aromatic at the range (1519.31) cm⁻¹ and the emergence of the C=O group of the carbonyl group at the range (1755.87) cm⁻¹, as well as the emergence of the aliphatic C-H type bend at the range (1051.61) cm⁻¹ and at the range (627.07) cm⁻¹, as well as the appearance of a C-Cl bundle at the range (781.66) cm⁻¹, as shown in figure (10). As for adding the engine oil consumed to the model at a rate of (8%), a slight displacement occurred and the chemical composition did not change, but a physical change also occurred and evidence of the presence of an aliphatic C-H type at the range (2983.19) cm⁻¹, as well as the presence of a type C=C aromatic atomizer at range (1519.59) cm⁻¹ and the emergence of the C=O group of the carbonyl group at the range (1755.66) cm⁻¹ as well as the emergence of the aliphatic C-H type bend at the range (1051.04) cm⁻¹ and at the range (627.01) cm⁻¹ and the presence of a type C-H aromatic as well as the
emergence of a C-Cl bundle at the range (781.87) cm\(^{-1}\) as shown in figure 11. Figure 12 shows the FTIR spectrum of the industrial asphalt produced at the Doura refinery.

![Figure (7) FTIR absorption spectrum for natural asphalt](image1)

![Figure (8) FTIR absorption spectrum for modified asphalt at 2% waste oil](image2)

![Figure (9) FTIR absorption spectrum for modified asphalt at 4% waste oil](image3)
Figure (10) FTIR absorption spectrum for modified asphalt at 6% waste oil

Figure (11) FTIR absorption spectrum for modified asphalt at 8% waste oil

Figure (12) FTIR absorption spectrum for industrial asphalt produced at the Doura refinery

4 Conclusions:

1. This method can be used to recycle WEO that pollute the environment and harmful to humans and recycle them as useful materials in improving asphalt specifications to keep the Iraqi environment healthy.
2. Asphalt Heet can achieve both the Iraqi specifications (1196-88) of the first type and the international standards (ASTM D312 type A) which states the following: (It should be distinguished as a good adhesive and has the characteristics of self-healing and liquidity affected relatively. Surface temperature is used in inclined surfaces with a slope of no more than 4% (i.e. most of the usual surfaces of buildings, because most construction work does not have a slope of more than 4%, especially in Iraq where inclined surfaces are not used in buildings).

3. The chemical composition of asphalt extracted from the springs before addition is very similar to the model in which the oil is added being hydrocarbons, which indicates that no chemical reaction occurred but rather a process of mixing the components through a spectral survey in the ultraviolet and infrared regions where the same beams appeared chemical bonds and transitions, with only different density. This is agreed with the other studies.

4. Asphalt is an oil derivative, and its presence in springs may be an indication of the presence of an oil reservoir in it.

5 Recommendations:
   1- Investing the natural Asphalt after its modification and using it for building and construction purposes due to the large quantities formed. And expand studies on this topic.
   2- The necessity to pay attention to research related to the environment and safe recycling of waste as a threat to the environment as well as the economic returns resulting from the utilization of such waste.

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