INTRODUCTION

Introduction

Asphalt [1, 2]

Asphalt is a dark brown to black material mostly made of hydrocarbons. However, most asphalt used today comes from crude petroleum. Asphalt is the matter that remains after crude petroleum is distilled to produce fuels and lubricating oils.

The amount of asphalt in the crude sample range from few percent for light crude to about 60% for heavy crude. Asphalt's properties depend on the crude petroleum's chemical make-up and on the refining process (c.f. Fig. 1).

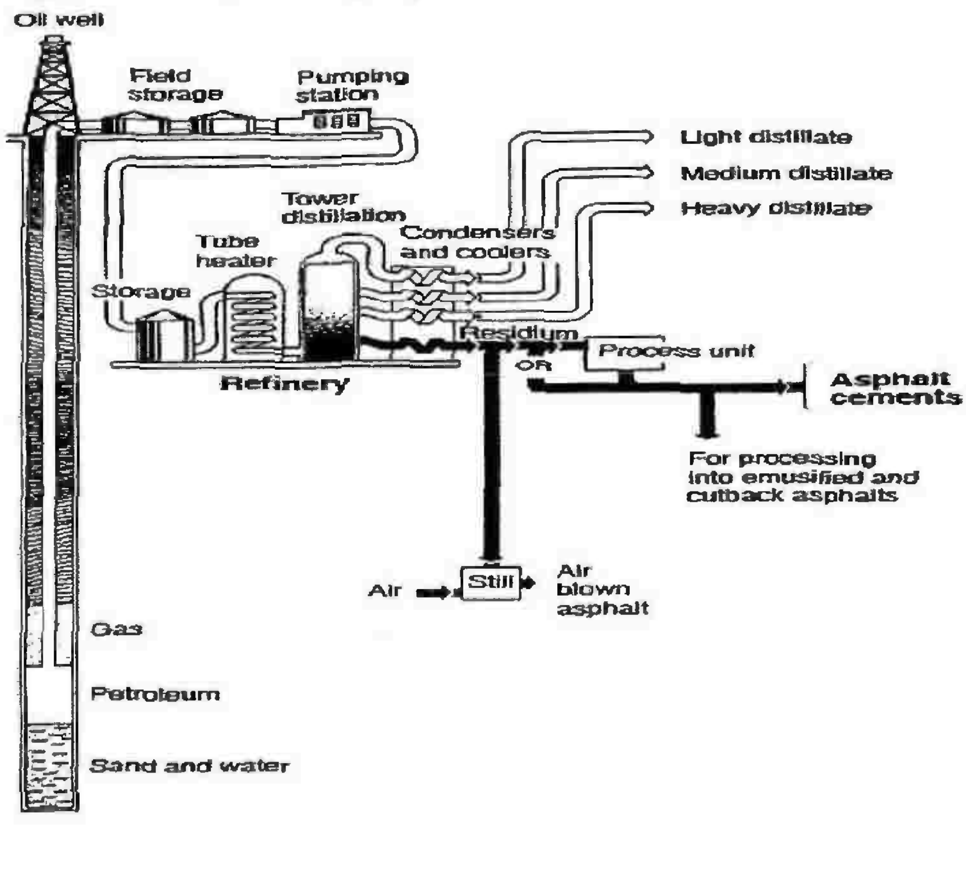


Figure 1: Production of asphalt from refining petroleum crude oil

Asphalt is valuable for construction because it is sticky, waterproof, strong, and durable. It is also highly resistant to many acids, alkalis and salts. People have known of asphalt's advantages at least since the ancient Mesopotamians when it was used about 5000 years ago to cement masonry and build streets, and to waterproof temple baths and water tanks.

It may even have been used as a water repellent in Noah's Ark. The first asphalt pavement was laid in Newark, New Jersey in 1870. Today asphalt is by far the most widely used paving material. About 96% of the 2.4 million miles of paved roads in the United States are paved with some type of asphalt. Not surprisingly, more than 85% of all asphalt produced today is used for paving applications.

The rest is used in buildings, agriculture, hydraulics, erosion control, industry, railroads, and other applications. Although asphalt is solid or semi-solid at normal air temperatures, it is produced in a variety of types and grades ranging from hard, brittle solids to almost water thin liquids. It is liquefied by heating, by adding a solvent (making a product called cutback), or by emulsifying with water and an emulsifier (creating a product called emulsion). As a liquid it can be sprayed directly on a surface or mixed with aggregate and sand. This bulletin describes the properties and uses of the three most common types of construction asphalts.

Asphalt Types [3, 4]

Three general types of asphalts are used in construction today: asphalt cement, emulsified asphalt, and cutback asphalt.

-Asphalt Cement:-

Also called paving asphalt, is a component of hot mix asphalt which is primarily used to construct flexible pavements (blacktop). This material is different from the other two types of asphalt because it is semi-solid and highly viscous (resistant to flow) at normal air temperatures. Asphalt cement is liquefied by heating then mixed with aggregates to produce hot mix. The mix is kept hot until it is spread on the road and compacted. Being very sticky, asphalt cement adheres to the aggregate particles and binds them together. After cooling to normal air temperature, hot mix makes a very strong paving material which can sustain heavy traffic loads. Asphalt cements are produced in different grades that vary in consistency or resistance to flow. To maintain acceptable consistency in pavements, softer grades are usually used in cold climates while harder grades are used in hot climates.

-Emulsified Asphalt:-

Emulsion, is made from asphalt cement. It consists of tiny particles of asphalt cement mixed with water and an emulsifying agent usually a detergent. Emulsions were first developed in the early 1900s and began being widely used in 1920s for dust control. Emulsions are called liquid asphalts because, unlike asphalt cements, they are liquid at normal air temperatures and therefore do not require heat to liquefy.

To produce emulsions, hot asphalt cement and water containing the emulsifying agent are pumped at high pressure through a colloid mill.

The emulsifying agent coats the asphalt particles and puts an electric charge on their surfaces. This charge causes the asphalt droplets to repel one another so they don't combine. These charges are used to categorize emulsions as cationic (positive charge) or anionic (negative charge).

Charges are important because they affect the compatibility of emulsion with mineral aggregates. An anionic emulsion should be used with limestone, and dolomite aggregate that usually bears a positive surface charge. A cationic emulsion should be used with siliceous gravel and sandstone because these aggregates usually bear a negative surface charge.

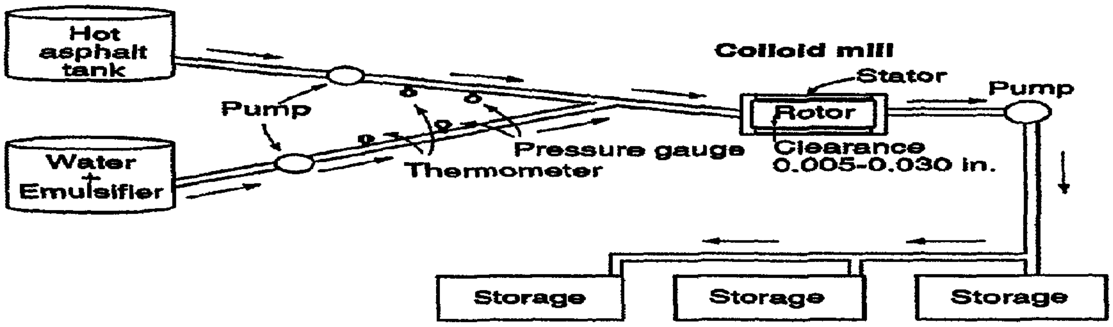


Figure 2: Manufacture of emulsified asphalt

After an emulsion is mixed with aggregates it sets or breaks. The asphalt droplets react with the aggregate and coalesce or combine, squeezing out the water. The water then evaporates, leaving the asphalt droplets to set and produce a continuous film on the aggregates. All emulsions are further graded according to their setting rate;

-Rapid setting (RS), Medium setting (MS), and-Slow setting (SS).

The type and amount of emulsifying agent controls the rate of setting. Select and use emulsions according to their setting rates. ASTM Standard D3628 recommends that RS emulsions be used for seal coats and penetration macadam pavements. The MS emulsions are recommended for open-graded cold asphalt-aggregate mixtures. SS emulsions are used for tack coats, slurry seals, and dense-graded cold asphalt-aggregate mixtures.

-Cutback Asphalt:-

Is liquid asphalt that can be used at normal air temperatures without heating. Cutbacks are produced by adding (cutting back) petroleum solvents to asphalt cements instead of water. Cutback asphalts set when the solvent evaporates after being applied to the aggregate. The evaporation rate depends on the type and amount of solvent used in the cutback. Cutbacks have three grades based on relative evaporation rates:-

-Rapid-curing (RC) is produced by adding a high volatility solvent such as gasoline or naphtha.
-Medium-curing (MC) is produced by adding an intermediate volatility solvent such as kerosene.
- Slow-curing (SC) is produced by adding an oil of low volatility such as diesel or other gas oil.

RC cutbacks set faster than MC which in turn set faster than SC. Cutbacks come in different grades that vary significantly in their consistency (c.f. Fig.3).

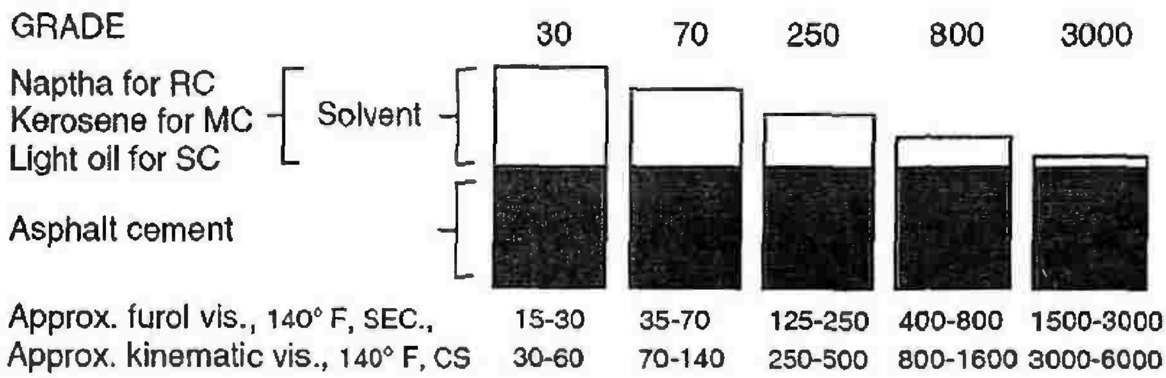


Figure 3: Composition of cutback asphalts

Cutbacks are increasingly being replaced by emulsions due to environmental regulations and other concerns. Emulsions release far fewer volatiles into the atmosphere and aren't as wasteful of high-energy, high cost products. Cutbacks have low flash points and are less effective than emulsions when applied to damp aggregate, pavements or soils.

-Blown Asphalt (5):-

Resin fractions consists of considerable unsaturated hydrocarbon constituents, the cycles that are present (as in the case of asphaltenes). The resins from asphalts may be hydrocarbonated to oils with hydrogen under pressure (6). Those fractions of asphalt may be dehydrogenated by so-called "oxidation" reactions to the next higher molecular weight material. Commercially, air (oxygen) is commonly used for blowing asphalts. The reaction is not one of oxidation but of dehydrogenation during which little or no oxygen is found to enter the molecule. Other elements also, which are in the same periodic group as oxygen, such as sulfur, selenium cause similar dehydrogenation reactions.

The action of free sulfur also forms complex sulfides, disulfides, and thio-ether. Sulfur appears particularly reactive with this type of asphaltic-resinous material as well as with olefins, some aromatics, and much paraffin, such as paraffin wax.

The action of oxygen in the air blowing of asphalts has been widely investigated (7, 8).

The reaction that takes place follows a sequence such as

$$H_3C\text{—}CH_3 + O \longrightarrow H_2O + H_2C{=}CH_2$$

Chemistry of Asphalt

Asphalt are complex mixtures of hydrocarbon contain atoms of oxygen, nitrogen, sulfur, and other metals such as nickel and vanadium in the form of heteroatoms or polar groups which indicate the existence of complex condensed structure.

The various hydrocarbons are classified as:-

-Aliphatic hydrocarbons -Aromatic hydrocarbons

-Heterocyclic compounds

-Aliphatic hydrocarbons:-

The aliphatic hydrocarbons are the chain type materials and may be either saturated or unsaturated. These materials are further classified as follows.

*Open chain hydrocarbon

i- Alkanes or Paraffin

a) Straight-chain hydrocarbons

Example: Octane $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

b) Branched-chain hydrocarbons

Example: 3-methyl pentane $CH_3\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}CH_3$

$\quad CH_3$

ii- Alkenes, unsaturated hydrocarbons

Example: 2-butene $CH_3\text{-}CH{=}CH\text{-}CH_3$

iii- Alkynes, Acetylene

Example: acetylene $CH{\equiv}CH$

** Closed-chain hydrocarbons

i- Cycloalkanes or naphthens

Example: cyclohexane $/CH_2\text{-}CH_2\text{-}/CH_2$

$CH_2\text{-}CH_2\text{-}CH_2$

ii- Cycloalkenes

Example: cyclohexene $/CH{=}\ CH\text{-}/CH_2$

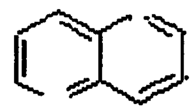
$CH_2\text{-}CH_2\text{-}CH_2$

-Aromatic hydrocarbons

The aromatic hydrocarbons are referred to as ring compounds and may be classified as follows:-

a) Mononuclear aromatic hydrocarbon,
for example: benzene

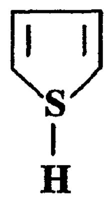
b) polynuclear aromatic hydrocarbons
Example naphthalene



-Heterocyclic compounds

The heterocyclic materials have two or more kinds of atoms in cyclic nuclei. It is in this type of compounds that nitrogen, sulfur, and oxygen are incorporated in asphalt.

For example: Thiophene



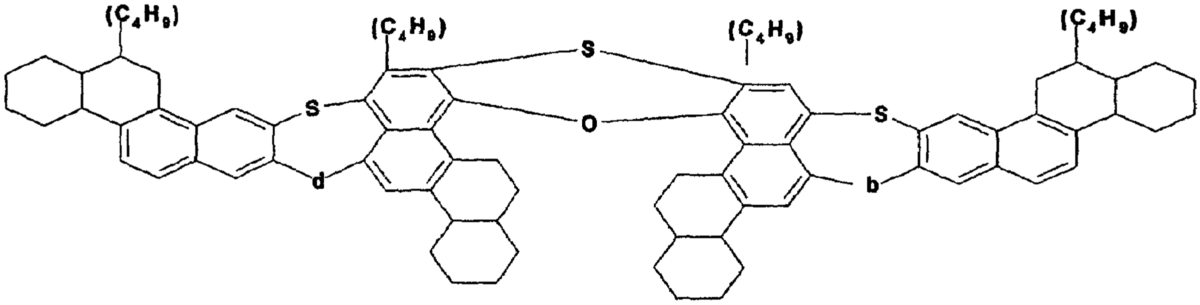
Asphalt Composition

The asphaltic components of petroleum are separated by a light hydrocarbon solvent into soluble maltenes portion and insoluble asphaltenes. The term 'maltene' denotes a mixture of the total resins and oils obtained as filtrates from asphaltenes precipitation, the structure and properties of these two portion vary; not only with crude oil source, but also with the type of solvent used for this precipitation.

Oils: The oily component is the fraction that soluble in cyclohexane with which it can be eluted from alumina. It consists of paraffinic straight chain, and cyclo paraffin and aromatic componenets. The paraffinic constituents are the fractions soluble in petroleum ether 40-60 °C boiling range (aromatic and sulfuric free); but is adsorbed on alumina and eluted by benzene. The oil fraction has the lowest percentage of heteroatoms, especially that containing sulfur and oxygen.

Resins: The term resin denotes the materials eluted from various solid adsorbents (silica gel and alumina) after oil elution they have an aromatic character, and do not contain any pure paraffinic or naphthenic hydrocarbon, their molecular weight are much higher than those of the oil.

Asphaltenes: Present in asphalt in the form of hard, solid, friable, brown-black constituents, which are the heaviest compounds of the condensed structure. Asphaltene are the high molecular weight materials and are primarily of an aromatic nature with very few side chains attached, it will be noted that sulfur and nitrogen are incorporated in the ring structure in this type of material



a, b,d represent points where neighboring nuclei could easily condense or cyclisize structure in three-dimensions. $C_{84}H_{98}OS_3$ Mol. Wt.= 1216
structure of asphaltene.

Waxes: is an extract obtained oils organic solvents. It is a mixture of organic hydrocarbons, petroleum waxes are generally classified as paraffin wax and microcrystalline wax.

Modification of Asphalt[9]:

The durability of asphalt pavement is greatly influenced by the environmental changes during the year, especially between summer and winter, and between day and night, when the daily average temperature change can be considerably large. In summer, the high temperature can soften the asphalt binder and consequently reduce the stiffness of the paving mixture. On the other hand, in winter the low temperature can stiffen the asphalt binder and reduce the flexibility of the paving mixture. As a result, thermal cracking may develop that adversely affects the performance and lifetime of the pavement. Thus, high-temperature stiffness and low- temperature flexibility are important properties that increase the lifetime of pavement [10].

Polymer modification causes significant changes in the stress-strain behavior. If a polymer is added to asphalt, the physical properties of the finished products may be very different.

Polymer –modified asphalt cement increases the level of field performance of asphalt concrete. Polymer modifiers, improve

(1)Thermal cracking resistance, (2) Provide resistance to permanent deformation. (3) Improve resistant to moisture damage (4) Decrease the temperature susceptibility of asphalt (hypothesized that improving the binder stiffness at high service temperatures and reducing stiffness at lower service temperatures develop overall improved binder) cements and increase the tensile strength of asphalt [11].

The polymer should form a continuous network within the asphalt, for this reason the polymer and asphalt need to be compatible, but the influence of the polymers depends on:-

(1) Physical properties, (2) Chemical properties.

(3) Quantity, and (4) Type of polymer.

Compatibility of The Mixture's Component [12].

The inability of polymers to mix with asphalt in an unlimited fashion is a rather general phenomenon. The behavior of asphalts under the influence of polymer additives has not yet been completely explained. It is generally accepted that asphalt-polymer systems are heterogeneous mixtures of varying character and degree of compatibility of their components. Choosing the proper components for these mixtures is not simple, because of the difficulties related to their miscibility. Prepared mixture should be at least micro hetrogeneous. Using the concept of compatibility found a way to disperse polymer uniformly ensuring in asphalt a homogeneous material, as verified by its physicochemical properties.

Fundamental elements, which determine the likelihood of obtaining homogeneous asphalt-polymer mixtures, are:-

1. The polymer should swell or be soluble in aliphatic or aromatic solvent and should distinguish itself by having a structure similar to that of oils and asphalt resins. If the polymer does not display such characteristic, then a third component that mixes well with asphalt needs to be introduced.

2- It is most beneficial to introduce the polymer into the asphalt in the form of a latex or oligomer. It is usually necessary to break up hard and brittle polymer as a first step.

3- In the case of applications involving highly oxidized asphalt containing relatively small amounts of oil-based components, the polymer should be plastified by the addition of aromatic or naphthenic oils.

4- It is beneficial to mix polymers with asphalt at temperatures that will ensure the elimination of processes that might degrade or destroy the polymer. As a rule, the mixing temperature should not be below 150°C.

The miscibility of components of asphalt-polymer mixture is influenced by two factors [13]:-

1- The method by which the mixture is obtained. It is especially important to determine the proper choice of parameters, such as temperature, mixing time, and speed of mixing (external factors)

2- The second factor is related to the properties and structure of the asphalt (amount of oils and asphaltenes in asphalt, the crystallinity degree of asphalt) and the polymer, as well as the source and amount of the added polymer (internal factors).

Polymers [14, 15]

Polymers are materials of very high molecular weight and they are found to have multifarious applications in our modern society. They usually consist of several structural unites bound together by covalent bonds for example, polyethylene is a long-chain polymer; $CH_2CH_2CH_2\,CH_2$ OR $[CH_2.CH_2]_n$

Where n is the chain length of the polymer.

-Classification of Polymers:-

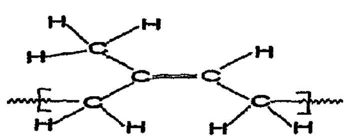
Classification is based on the response of the polymer to heating. In this group there are two types of polymers:

Thermosetting Polymers and Thermoplastic Polymers

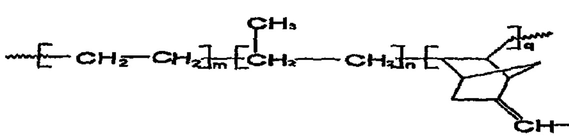
Thermosetting polymers are set or hardened on heating (curing), into a permanent shape due to an irreversible cross-linking reaction. On the other hand thermoplastic polymers, do not undergo any permanent change on heating and, therefore can be reshaped any number of times. The most commonly used thermosetting resins are, polyurethane, silicone resins, and epoxy resins.

Rubbers:

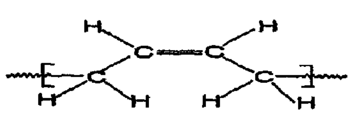
Rubbers form one of the most important groups of commercial polymers and may be considered as a special class of plastic materials, which possess recoverable high elasticity. However, the use of these materials is not restricted to applications in which recoverable high elasticity is a requirement. Because of the high elasticity of rubber materials, they cannot be shaped by molding or extrusion. In 1820 Thomas Hancock in the UK discovered that if the rubber was masticated, it becomes plastic and hence capable of flow. In 1839 Charles Goodyear in the USA and Thomas Hancock also found that the plastic masticated rubber retained its elasticity upon heating with sulfur over a wide range of temperature with greater resistance to solvents than the raw material. The rubber-sulfur reaction was termed "Vulcanization" by William Brockendon. In extensions of this work on vulcanization, which normally involved only a few percentage of sulfur, in the 1940s both Goodyear and Hancock found that if rubber was heated with larger quantities of sulfur (about 50 parts per 100 parts of rubber) hard product was obtained.This subsequently became known variously as ebonite, vulcanite and hard rubber [16]. This type of hard rubber (Ebonite) is still important. Its characteristics include high resistance to chemicals, good electrical insulating properties, and the ability to be machined easily. Some representative molecular sub units of rubbery polymers are:



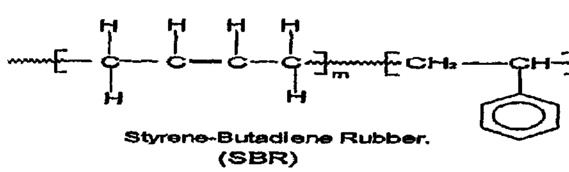
Cis-1,4-polyisoprene Rubber.
(NR)



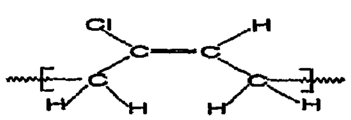
Ethylene-Propylene-Diene Terpolmer Rubber.
(EPDM)



Cis-1,4-polybutadiene Rubber.
(PBR)



Styrene-Butadiene Rubber.
(SBR)

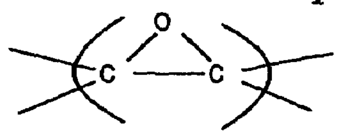


Cis-1,4-polychloroprene Rubber.
(CR)

Thousands of these units linked together into a chain constitute a typical molecule of these elastomers. Such molecules change their shape readily and continuously at normal temperatures by Brownian motion [17, 18].

Epoxy Resin [14]

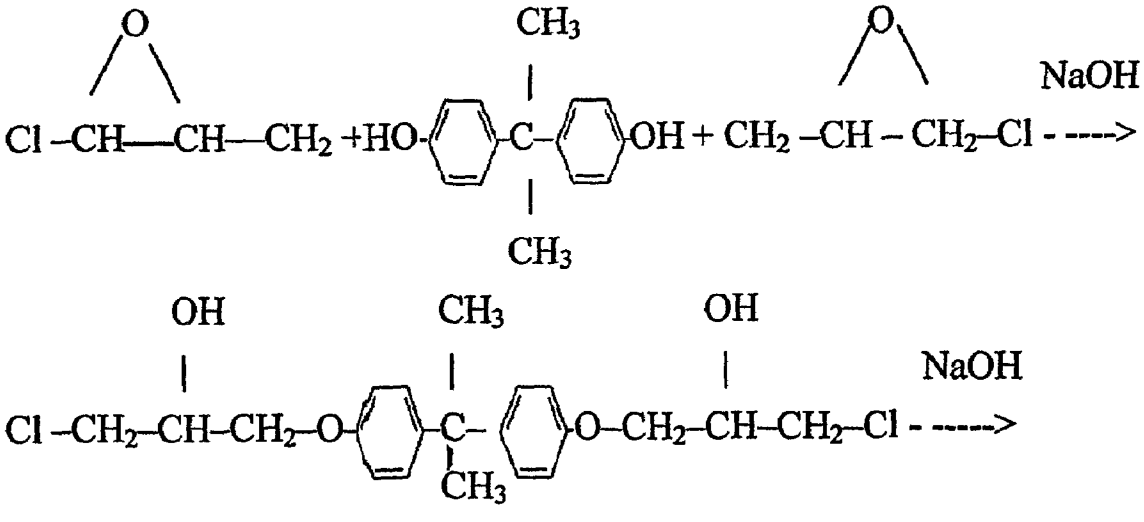
The word epoxy comes from the Greek prefix meaning (over) or (between) and the English suffix for oxygen. Thus an epoxy material may be regarded as oxygen between compounds. The term (epoxy resin) is applied to both the pre-polymers and to the cured resin. The former contains reactive epoxy group.

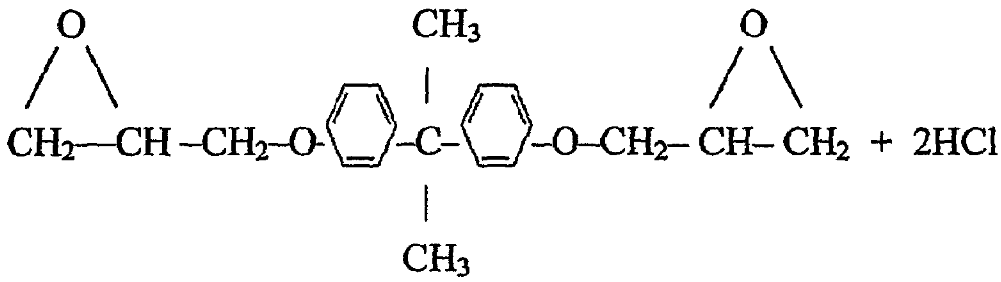


Epoxy resins are thermosetting viscous liquid or brittle solids. Epoxy resins are well known for their outstanding chemical resistance. They find wide applications, and the major applications of epoxy resins are in the field of adhesions,

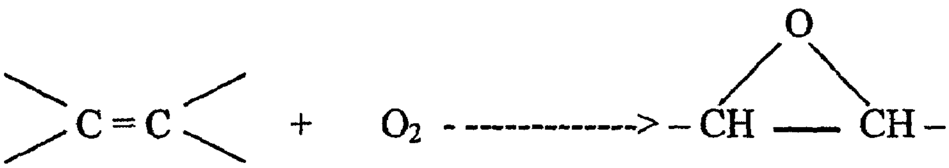
Manufacture of Epoxy Resins [19]

1- The most important class of epoxy resins; used at present on a large commercial scale, is that based upon the reaction between bisphenol and epichlorohydrin in the presence of alkali. The reaction proceeds as follows





2- Non-glycidyl-ether epoxy resin is one of the most important alternative ways of introducing the reactive epoxy group into the molecule. One of these is the epoxidation of unsaturated compound as shown below;



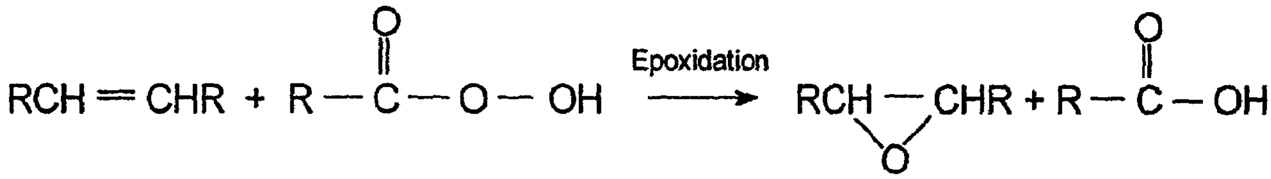
Unsaturated Compound Epoxy compound

Epoxidation of Olefins [20]:-

Epoxidation is the formation of cyclic three-member ethers (oxiranes) by the reaction of peracids and hydrogen peroxide with olefin and aromatic double bonds. The three-member ethers formed are also designated as 1, 2-epoxides.

Epoxidation Processes

The epoxidation processes can be divided into two basic types: either the peracid is preformed or it is formed in situ, i.e. in the primary reaction vessel.



Alkene Peroxy acid Epoxide or (Oxirane) Acid

Epoxidation with Preformed Peracid Process

The peroxidation of acetic acid with hydrogen peroxide is carried out at high molar ratios of acid/hydrogen peroxide; however, large amounts of acetic acid must be removed if high ratios are involved. In addition, concentrations of peracetic acid above 40-45 wt% in acetic acid are explosive at epoxidation temperatures, and therefore, related epoxidation processes require large volume production on an essentially continuous basis since the preformed peracid cannot be safely stored. Epoxidation with preformed peracetic acid does not necessarily utilize a catalyst at 20-80 °C

-Properties of Epoxidized Rubber:-

Epoxidized natural rubber has several improved properties in vulcanizates such as better oil resistance, resilience and lower gas permeation than those of natural rubber [21, 22]. The 50% epoxidized natural rubber shows very interesting physical properties and excellent carbon black dispersion [16]. It has similar oil resistance as nitrile rubber and a higher tensile strength. It has also reduced gas permeability as in butyl rubber [23]. Epoxidation of natural rubber improves its heat resistance [24].

Vulcanization [25-27]:

It is the process of converting the thermoplastic polymer to thermosetting material having three dimensional networks, by using vulcanizing agents. Vulcanization may be done chemically (sulfur vulcanization) by sulfur (the most used), selenium, tellurium, and oxygen, or done by radiation with gamma-rays.

When sulfur reacts with two rubber macromolecules, it adds on at the point of opening of double bonds to form a so-called sulfur bridge.Vulcanization reaction may also occur without opening of double bond, this such as vulcanization reaction of polychloroprene by metallic oxides (as ZnO).

Free radical vulcanization also may occur for saturated rubber as silicon rubber, which cannot vulcanize by sulfur for absence of double bonds. Formation of free radical may be by radiation or by addition of decomposes compound by heat as benzoyl peroxide.

Casting [25]:

Since the mid-1950'S, electrical-equipment manufactures have taken advantage of the design freedom afforded by epoxy casting techniques to produce switchgear components, transformers, insulators, high voltage cable accessories, and similar devices.

In casting, a resin-curing agent system is changed into a specially designed mold containing the electrical component to be insulated. After cure, the insulated part retains the shape of the mold.

In encapsulation, a mounted electronic component such as a transistor or coil windings, laminates, lead wires, etc, are impregnated with the epoxy system. Potting is the same procedure as encapsulation except that the aluminum mold is a part of the finished unit. In dipping, a component is simply dropped into a resin-curing agent system and cured without a mold. It provides little or no impregnation and is used mainly for protective coatings.

The choice of epoxy resin, curing agent, fillers, and other ancillary materials depends on factors such as processing conditions and the environment to which the insulated electrical or electronic component will be exposed. Amount of filler that can be incorporated into the system depends on the viscosity of the resin at the processing temperature. Viscosity can be modified by heat or a reactive diluent's; heating is preferred since diluents affect system properties. Amine curing agents are used in small castings, and anhydrides in large castings. Anhydrides are less reactive and have lower exotherm than amines. In addition, their viscosity and shrinkage are low and pot lives are longer. For most epoxy-based tooling formulations, aliphatic polyamines are used for ambient temperature cure, and modified aromatic diamines for hot cures. Diluents, toughening agents, and filler are added when required.

Cured epoxidized natural rubber is one such rubber, which gives several improved properties such as excellent adhesion to a variety of substrates; better oil resistance, thermal stability; and lower gas permeation than those of natural rubber [28].

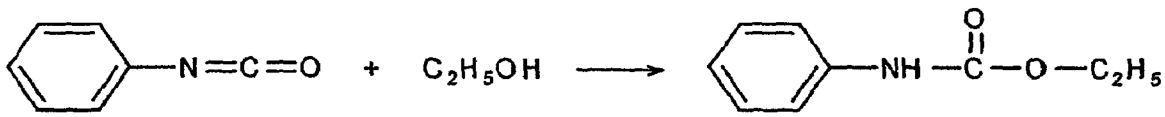
Polyurethane [29, 30].

Polyurethane is a generic term, it designates a polymer where in the repeating unit is a urethane linkage. The latter is obtained by reaction of a polyisocyanate with compounds containing two or more hydroxy1 groups per molecule.

Polyurethanes (or simply urethanes) have been used for about thirty years as surface coating media. They posses many desirable properties but their commercial development was retarded by two factors.

One being a two component system and the other being a health hazard because of the vapor present. Later development improved both problems :

The urethane reaction was discovered by Wurtz [31] in 1848. He reacted an isocyanate with alcohol to produce a urethane :



Properties of Urethane [29]

The essential component of all urethane-based products is isocyanate. Isocyanates contain one or more N=C=O groups. This group reacts with organic compounds containing active hydrogen atom, such as – OH, -NH-SH-NHR, and COOH radicals.

The most important reaction is with hydroxyl- bearing components as follows :

$$R—NCO + R^{\backslash}OH \longrightarrow R—NH—\overset{O}{\overset{\|}{C}}—OR^{\backslash}$$

By using polyfunctional reactants, that is by reacting compounds containing two or more isocyanate groups with compounds containing two or more hydroxyl groups, it is possible to build polymercic materials

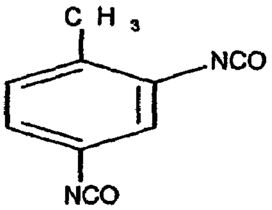
$$HO—R—OH + OCN—R^{\backslash}— NCO \longrightarrow HO—R—(O—\overset{O}{\overset{\|}{C}}—NH—)R^{\backslash}—NCO$$

Urethane groups.

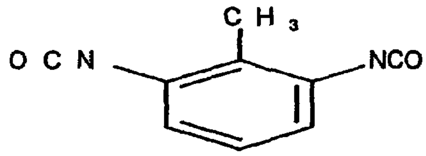
Moisture and carboxy groups are always present in a polyol to some extent, the isocyanate will react with them.

The first commercially available diisocyanate was toluene diisocyanate (TDI). Today it is produced in greater quantities than all other isocyanates combined. It is the prime isocyanate used for flexible foams.

TDI is available in two isomeric forms, 2, 4 and 2, 6 tolylene diisocyanate ; the former is more reactive. For surface coatings, the 2, 4 isomer or a mixture of 80% 2.4 isomer and 20% 2.6 isomer are most commonly used. There is also a 65/35 mixture of 2.4 and 2.6 isomers; it is less reactive and not commonly used for surface coatings



Tolyene 2, 4 diisocyanate



Tolylene 2, 6 diisocyanate

Polyurethane in Asphalt [32].

A novel process for producing asphalt-blended polyurethane foam has been developed by using conventional raw materials of polyurethane and asphalt to be used as sealing materials in vehicles and civil engineering, and as sound and vibration damping materials in vehicles and general industries.

One component moisture cured elastic polyurethane sealants [33] are among the premier sealants of the 1980's mainly because of their excellent mechanical and weatherability. They are used in construction, civil engineering and ship of yacht building to fill joint of concrete, wood, glass, aluminum and plastics and the machine and automobile industry to seal metal parts [34]. In commercial formulations, isocyanate-terminated pre-polymer, that is the substantial part of the product, is usually mixed with mineral or carbon fillers, thixotropic agents, plasticizers, resins, etc. Especially interesting for the sealant formulator is the possibility of polyurethane modification with bitumens since in this way some new features of the product can be achieved and its cost can be lowered significantly. The poor compatibility of the components has been overcome either by high temperature blending of urethane pre-polymer with melted asphalt [35] or by reacting substrates for polyurethane directly in melted asphalt [36]

Application

Polymer can induce various changes in asphalt properties, as determined by the possibilities of their versatile applications. Asphalt

* In the machine industry, as anticorrosive coatings and as materials to suppress vibrations and absorb sounds.

* Asphalt is also used to stabilize soils, for impregnation on cartons, as glues, and binders to connect steel to wood.
* Replacements for specific type of polymers for roads and industry. They are distinguished by markedly improved thermo rheological and strength qualities when compared to unmodified asphalt or to petroleum by-products.

*Polymer mixtures are found for certain applications such as modified asphalt roofing or pavement, they are used as:-
• Tack coat to ensure bond between new and old surface.
• Fog seal to seal small cracks and surface voids and renew old asphalt surfaces that have become dry and brittle with age.
• Prime coat to prepare a granular base for an asphalt mix surface course by strengthening, waterproofing and improving adhesion.
• Dust palliative to keep dust down and make a road passable in bad weather.
• Mulch treatment to temporarily stop soil erosion during vegetation growth. Several grades and types of asphalt are suitable for each type of construction. Choosing the grade depends mainly on climate conditions at the job site. Colder sites usually require softer grades of asphalts.

I. F. Gladkikh et al [(37)] illustrated the formation of asphalt-resin oligomers by reaction of petroleum vacuum residues and bitumens with the oligoisoprene fraction from the dimethylformamide distillation bottoms (isoprene production waste) were studied by thermomechanical and thermogravimetric analyses. The number-average molecular weights of the final product and initial components were determined

M. A. MULL et al[38] illustrated that the fracture resistance of chemically modified crumb rubber asphalt (CMCRA) pavement was evaluated based on the *J*-integral concept. The chemical modification process used was developed by the Federal Highway Administration and patented in 1998. The results were compared to that of crumb rubber asphalt (CRA) and control asphalt pavement. Four semi-circular core specimens (76 mm radius and 57 mm thickness) were cut from each gyratory compacted cylinder (GCC) for the fracture resistance tests. Notches with different depth to radius ratios were introduced at the middle of the flat surface of each specimen. Three point bend loading was used to allow the separation of the two surfaces due to tensile stresses at the crack tip. It was found that the CMCRA pavement, had the highest residual strength, at all notch depths tested. The fracture resistance of the CMCRA pavement, based on *J*c was found to be about twice that of the CRA and control pavements. The CRA pavement was found to have a slightly higher fracture resistance than that of the control pavement. Scanning Electron Microscopic examination of the fracture surface of each mixture revealed the microstructural origin of the improved fracture resistance of the CMCRA pavement in comparison with the control pavement.

G. D. AIREY [39] illustrated the polymer modification of road bitumens with SBS. Six polymer modified bitumens (PMBs) were produced by mixing bitumen from two crude oil sources with an

SBS copolymer at three polymer contents. The rheological characteristics of the SBS PMBs were analysed by means of dynamic mechanical analysis using a dynamic shear rheometer (DSR). The results of the investigation indicate that the degree of SBS modification is a function of bitumen source, bitumen-polymer compatibility and polymer concentration. When the polymer concentration and bitumen-polymer compatibility allow a continuous polymer network to be established, modification is provided by a highly elastic network which increases the viscosity, stiffness and elastic response of the PMB, particularly at high service temperatures. However, ageing of the SBS PMBs tends to result in a reduction of the molecular size of the SBS copolymer with a decrease in the elastic response of the modified road bitumen.

D. G. Shunin [(40)] illustrated the procedures that are discussed for production of rubber-bitumen compounds based on spent rubber items. A possibility of using these binders for paving is studied experimentally.

V. V. Leonenko and G. A. Safonov [(41)] illustrated the modification of petroleum asphalts with polymeric materials was examined. Polymers containing a crystalline phase can be used as modifiers. Based on an adsorption model of the reaction of the polymer with the disperse phase of the asphalt, a relation was obtained for determining the lower concentration of cross-linking of the polymer in the polymer–asphalt composite. It was shown that the total maximum content of asphalt in the polymer and disperse phase should not exceed 25%.

Weidong Cao [(42)] tried to *minimize* waste tires pollution and improve properties of asphalt mixtures, properties of recycled tire rubber modified asphalt mixtures using dry process are studied in laboratory. Tests of three types asphalt mixtures containing different rubber content (1%, 2% and 3% by weight of total mix) and a control mixture without rubber were conducted. Based on results of rutting tests (60 °C), indirect tensile tests (10 °C) and variance analysis, the addition of recycled tire rubber in asphalt mixtures using dry process could improve engineering properties of asphalt mixtures, and the rubber content has a significant effect on the performance of resistance to permanent deformation at high temperature and cracking at low temperature.

Chui-Te Chiu et al [43] illustrated the feasibility of using asphalt rubber (AR), produced by blending ground tire rubber (GTR) with an asphalt, as a binder for stone matrix asphalt (SMA). Two different sizes of GTR produced in Taiwan were used. The potential performance of AR–SMA mixtures was also evaluated. The results of this study showed that it was not feasible to produce a suitable SMA mixture using an asphalt rubber made by blending an AC-20 with 30% coarse GTR with a maximum size of 0.85 mm. However, SMA mixtures meeting typical volumetric requirements for SMA could be produced using an asphalt rubber containing 20% of a fine GTR with a maximum size of 0.6 mm. No fiber was needed to prevent drain-down when this asphalt rubber was used. The AR–SMA mixtures were not significantly different from the conventional SMA mixtures in terms of moisture susceptibility from the results of AASHTO T283 tests. The results of the wheel tracking tests at 60 °C show that rutting resistance of AR–SMA mixtures was better than that of the conventional SMA mixtures.

Wong Cheuk Ching [44] illustrated the effects of different sizes of crumb rubber modifier (CRM) on the high temperature susceptibility of three gradations (AC-10, AC-20 and PA) of wearing course mixtures. A wet process and 10% CRM by total weight of binders were used in these studies and the control variables for these studies included three CRMs of sizes 0.15 mm, 0.30 mm and 0.60 mm. The evaluations were twofold. Firstly, a comparison of the properties of those modified and unmodified binders at a wide range of testing temperatures and ageing conditions was conducted. Secondary, a comparison of the rutting resistance of the CRM and conventional mixtures was made. The results show that all the CRMs have overall contributed to better performance of both binders and mixtures at high temperatures. In addition, among these three CRM sizes, mixtures modified with 0.15 mm CRM exhibited the best effect on the dense-graded mixture (AC-10 and AC-20) whereas mixtures modified with 0.60 mm CRM exhibited the best effect on the open-graded mixture of porous asphalt (PA)

Yetkin Yildirim (45) illustrated a review of research that has been conducted on polymer modified binders over the last three decades. Polymer modification of asphalt binders has increasingly become the norm in designing optimally performing pavements, particularly in the United States, Canada, Europe and Australia. Specific polymers that have been used include rubber, SBR, SBS and Elvaloy. Specifications have been designed and pre-existing ones modified to capture the rheological properties of polymer modified binders. The elastic recovery test is good at determining the presence of polymers in an asphalt binder, but is less successful at predicting field performance of the pavement

Piti Sukontasukkul (46) illustrated the recycling granulated waste tires (crumb rubber) that has been widely studied for the last twenty years mostly relating to applications such as asphalt pavement, waterproofing system, membrane liners, etc. In this study, the use of crumb rubber to replace coarse and fine aggregates in concrete pedestrian block was studied. It is believed that concrete acting as a binder mixed with crumb rubber can make concrete blocks more flexible and thus, provide softness to the surface. The crumb rubber block also performed quite well in both skid and abrasion resistance tests. The production process was economical, due to the simplicity of the anufacturing process

Ahmet Tortum et al (47) illustrated the taguchi method used to determine optimum conditions for tire rubber in asphalt concrete with Marshall Test. The tire rubber in asphalt concrete was explored under different experimental parameters including tire rubber gradation (sieve #10–40), mixing temperature (155–175 °C), aggregate gradation (grad. 1–3), tire rubber ratio (0–10% by weight of asphalt), binder ratio (4–7% by weight of asphalt), compaction temperature (110–135 °C), and mixing time (5–30 min). The optimum conditions were obtained for tire rubber gradation (sieve #40), mixing temperature (155 °C), aggregate gradation (grad. 1), tire rubber ratio (10%), binder ratio (5.5%), compaction temperature (135 °C), mixing time (15 min).

B.S. Cleland et al (48) illustrated that the participants completed 1600 trials over 20 objects on an instrumented racing cycle.
Recordings of lateral acceleration and handle bar angle were combined to form a single measure of instability and compared to recordings of normal riding over smooth asphalt. New techniques to control for learning effects were used within an experimental procedure that controlled for the angle and speed of the cyclist. Sixteen of the objects including rough ground, a round utility access cover, oversized thermoplastic lines (mm thick), and an audio-tactile line show significant effects on the stability of

cycles. Traditional chlorinated rubber lines, one thermoplastic line, and a waterborne line show no significant impact on cycling. Relative assessment of the effect of the objects on cycle stability is reported and the validity and reliability of the method is discussed

J. Navarro et al [49] illustrated the thermo-rheological behaviour at in-service and handling temperatures (i.e. pumping, mixing, compaction, etc.) of bitumens modified by 9 wt% crumb tire rubber. The use of waste tire rubbers as bitumen modifiers can contribute to alleviate pollution problems derived from discarding scrap tires. Thus, the mechanical characteristics and storage stability of crumb tire rubber modified bitumens (CTRMBs) have been studied as a function of rubber particle size. The addition of ground tire rubber to bitumen increases both the linear viscoelastic moduli and viscosity, at high in-service temperatures, and reduces the storage and loss moduli, at low temperatures, resulting in a more flexible binder in this temperature region. As a consequence, crumb tire rubber modified bitumen displays enhanced mechanical properties, which improves its resistance to both rutting and fatigue cracking. The presence of insoluble non-spherical particles affects the flow behavior observed at high temperatures. From the experimental results obtained, it may be concluded that the use of rubber particle sizes lower than 0.35 mm and high shear rates during manufacturing operations is highly recommended. Storage stability of CTRMBs decreases with increasing particle size and storage temperature and takes place by the precipitation of the non-dissolved rubber particles. Only the sample containing rubber particles with a mean particle size of 0.29 mm remains stable under the selected storage conditions.

R.D. Lisi et al [50] illustrated the Markets for scrap tires have expanded since the early 1990s with the development of value-added applications such as tire-derived fuel and crumb-rubber-amended asphalt. Granulated tires have also displayed the ability to adsorb volatile organic compounds, indicating that the rubber material can be a useful filter media. Sand-based root zones, typically used for golf course putting green and athletic field construction, lack sufficient cation exchange capacity to restrict nitrogen and phosphorus migration through the root zone and into sub-surface drainage systems. Therefore, the adsorptive properties of tire rubber for retaining nitrogen and phosphorus were studied when applied as a distinct sub-surface drainage or intermediate layer in golf course putting greens. A statistically significant reduction in the concentration of nitrate in leachate was achieved by replacing traditional pea gravel with equally sized granulated tires for the drainage layer media, although the mechanism of nitrate mitigation remains unclear. The results indicate that using granulated tires as a drainage layer or fill material beneath sand-based root zones does not compromise the function of the profile or quality of the vegetation while creating an environmentally beneficial and value-added option for scrap tire reuse.

Yonghong Ruan et al [51] illustrated the effect of long-term aging on rheological properties of polymer modified asphalt binders. Modifiers included diblock poly (styrene-b-butadiene) rubber, triblock poly (styrene-b-butadiene-b-styrene), and tire rubber. Asphalt aging was carried out either at 60 ^{o}C in a controlled environmental room or at 100 ^{o}C in a pressure aging vessel [AASHTO Provisional Standards, 1993]. Both dynamic shear properties and extensional properties were investigated. Polymer modification resulted in increased asphalt complex modulus at high temperatures, decreased asphalt complex modulus at low temperatures, broadened relaxation spectra, and improved ductility. Oxidative aging decreased asphalt temperature susceptibility, damaged the polymer network in binders, further broadened the relaxation spectrum and, diminished polymer effectiveness in improving asphalt ductility

Xuejun Zhang et al (52) illustrated that several techniques have been used to minimize the problems caused by paraffin deposition, and internal coating is considered an attractive technological alternative. In this work, the influence of the eight coatings, such as polyvinylidene fluoride (PVDF), silicone rubber, methyl acrylate-stytene copolymer (MAS), polyurethane (PU), epoxy resin (EP), on drag reduction and paraffin deposition prevention is evaluated by rotation viscometer and cold spot. The wettability characteristics, the advancing and receding contact angles between coating surface and ozocerite or crude oil were measured by the Wilhelmy plate method. A correlation between both results was also obtained. According to the dynamic contact angle and the hysteresis factor of the resin coatings against asphalt, ozocerite and crude oil, the properties of drag reduction and paraffin deposition prevention on coatings were briefly discussed. The wetting characteristics of the surface have a significant influence on the amount of paraffin deposited and shear force. The low surface energy of fluoroethylene polymer, silicone rubber and methyl acrylate-stytene copolymer coatings, which have obvious effect on drag reduction and paraffin deposition prevention, can increase the advancing contact angle and hysteresis factor and decrease the steel surface wettability against asphalt, ozocerite or crude oil. The great hysteresis factors of coatings against asphalt, ozocerite or crude oil may have an important effect on the inhibition of paraffin deposition and drag reduction in crude oil

A.P. Kuriakose et al [53] attempted at the utilisation of the oily sludge, which is a dumped waste of petroleum refineries. Growing public concern over the health and environmental implications of these wastes has forced the regulatory agencies to make it mandatory for these industries to undertake the disposal of these wastes in an effective and environmentally safe manner. In the present work, the above sludge after purification was subjected to vacuum distillation to recover approximately 17% of lighter oils. The residue was subjected to heat treatment at 225 °C for 2.5 h with '2.5% w/w AlCl3' to obtain industrial bitumen 90-15 grade ŽIndustrial bitumen are of different types depending on the softening point-penetration relationship. The first figure 90 represents the softening point while the second figure 15, represents the penetration. Both penetration and softening points are a measure of consistency for bitumen.. The usefulness of the above industrial bitumen was tried in the preparation of bituminous paints. All three formulations investigated were found to be homogeneous showing no separation of solvent. There was no coagulation of the asphalt base nor settling or packing in the container. These samples were found to meet the requirements of drying time, consistency, finish, stripping, flexibility and adhesion, keeping properties, etc. It was also seen that the heat resistance of these bituminous paints can be increased considerably by including cashew nut shell liquid_formaldehyde resin in the formulation. Cashew nut shell liquidŽCNSL.is a cheap by-product of the cashew industry, and its utilisation can also help to reduce production costs of bituminous paints. This study also showed that incorporation of chlorinated rubber in the formulation would enhance the acid resistance considerably without affecting heat resistance and other desirable properties. This method of using sludge as bituminous paints can be a simple, eco-friendly and useful means of disposal in petroleum refining industries.

Francis P. Miknis and Laurent C. Michon [54] illustrated that the Nuclear magnetic resonance (NMR) imaging methods have been applied to study the behavior of crumb rubber materials in asphalt. Pieces of natural tire rubber and styrene-butadiene tire rubber were immersed in high acid content asphalt and heated at 170°C for different periods of time up to 48 h. After heating, 3D images were acquired during cooling and after the samples were at room temperature. Images of the natural and styrene butadiene rubber in asphalt, taken at room temperature after heating, showed a progressive loss of image intensity with increased heating time. From an NMR perspective the loss of signal could be due to the rubber having become more rigid as a result of heating, or because of possible dissolution of the rubber by the asphalt. However, images of the same samples, taken while the samples were at an elevated temperature, showed that the crumb rubber materials had swelled in the presence of the asphalt. Samples of the same materials in the absence of asphalt were heated and imaged in the same manner. Images of these samples showed only a small loss of signal with heating and hardly any swelling.

Pavment Asphalt:-

All asphalt pavements are a combination of mineral aggregate and asphalt material constructed in various thickness and types. The asphalt serving only as a cementing agent to bind the aggregate in proper position to transmit the applied wheel loads to underlying layers where the load if finally dissipated. The aggregate is usually crushed stone, limestone, dolomite, basalt, gravel, slag, and used either in combination with on other or single

Types of asphalt pavements

Are called asphalt concreate mix, is used in two ways:-

1- Mixed with aggregates at plants then heated to the paving site and compacted on the road, or
2- Sprayed in relatively thin layers with or without aggregates

Class1- Plant Mixes.
Are called asphalt concreate mix. These can be produced and laid down hot, using asphalt cements, or cold, using emulsion or cutbacks. These mixes usually contain about 5% asphalt and 95% aggregate by weight. Aggregate give the mix most of its ability to carry or resist loads while the asphalt coats and binds the aggregate structure

Hot Laid Mixes, also called hot mix asphalt, are produced by mixing heated aggregates and asphalt cements in special mixing plants. These very strong, stiff mixes are usually used for surface and subsurface layers in highways, airports, parking lots, and other areas which carry heavy or high volume traffic.

Cold Asphalt Mixes are produced by mixing damp, cold aggregates with emulsions or cutbacks at mixing plants, either stationary plants or portable ones brought to the site. Although not as strong and stiff as hot mix, cold mixes may be more economical and flexible, and less polluting. They are used for areas with intermediate and low traffic, for open graded mixes, and for patching.

Class2- Penetration or Layered System

Sprayed asphalt include asphalt-aggregate applications, usually called surface treatments or seal coats, and asphalt-only applications such as tack coat, prime coat, fog seal, and dust prevention. Surface treatments and seal coats usually include one or more applications of asphalt and aggregate which are less than 25 mm (1 in.) thick each. Examples are sand sea, chip seal, double and triple seal, and slurry seal. A single seal involves spraying an asphalt product and following at once with a thin (3/8in.) aggregate cover. The cover is rolled as soon as possible socthat two-third of the aggregate depth is embedded into the asphalt layer. For multiple seals, the process is repeated a second or third time. Each succeeding time the aggregate should be about half the size of that used in the previous layer.

Slurry seal is different from other sprayed applications because the asphalt emulsion is mixed with the aggregates in a special truck mixer just before spreading.

Pavement maintenance and rehabilitation [2,55, 56]**:-**

Asphalts play a major role in maintaining and rehabilitating pavements. For every type of pavement failure (distress) there is at least one asphalt type that can treat the damage. There are four major types of pavement failures: cracking, distortion, disintegration, and slippery surface. Cracking includes thermal, reflective, alligator, joint, edge, slippage, and shrinkage cracks.

Cracks create a rough surface which allows water to enter the base and sub-base and soften these layers and leads to pavement deterioration. Crack sealing is an effective maintenance treatment if done early in the life of the pavement. Pavement distortions include rutting, shoving, corrugations, settlement depressions, and frost upheaval. These are some of the most serious pavement failures because they require major patching, rehabilitation or reconstruction to bring the pavement to good condition.

Disintegration of the pavement surface includes raveling and potholes. Raveling is the progressive loss of surface material by weathering and/or traffic action. It is caused by poor construction, inferior aggregates, poor mix design, or aging of the asphalt. An early application of a fog seal can retard raveling. Extensive raveling may require a slurry, sand, or chip seal depending on the surface condition and traffic.

Slippery surfaces are also a major concern because they make the pavement unsafe for vehicle stopping and maneuvering. They are caused either by excess asphalt or by polishing of aggregates.

Bleeding or flushing is the result of excess asphalt in rich asphalt mixes, improperly constructed or designed seal coats, or a prime or tack coat which is too heavy.

Heavy traffic can force or flush asphalt to the surface. Also, hydrophilic (water loving) aggregates may cause the asphalt to strip off and migrate to the surface. Bleeding can often be corrected by repeated applications of hot sand, rock screenings, or coarse aggregates.

Aggregates, which should be larger than the asphalt film thickness, are rolled into the film. If bleeding is light, you may also apply a hot-mix asphalt friction course or an aggregate seal coat with absorptive aggregates. Traffic action polishes aggregates. The condition is common with certain types of weak aggregates. The only way to repair this condition is to cover the surface with a skid-resistant treatment. A thin overlay, a sand seal, or a chip seal with hard angular aggregates should be used.

Properties and specifications for aggregates and asphalts [57]

Selecting the proper types of asphalts and aggregates to construct a pavement or solve a pavement problem involves looking at different test results which describe their properties. Asphalt and aggregate are usually defined by a specification system which gives the range of properties needed to meet a certain grade.

Aggregates for asphalt mixtures

The amount of aggregate in an asphalt paving mixture is generally 90%-95% by weight or 75%-85% by volume. Asphalt pavement performance is heavily influenced by aggregates which carry most of the traffic loading. Their suitability for construction depends on size, gradation, toughness, cleanliness, shape, absorption, and affinity to asphalt. Size and gradation (mix of various sizes) are the most important.

When aggregates of different sizes are combined, then mixed with asphalt and compacted, the resulting structure should have a reasonable amount of voids. These voids, also called voids in the mineral aggregates (VMA), provide space for asphalt coating and for expansion from temperature changes.

Aggregates in the field are usually stockpiled in different sizes. These should include at least fine and coarse piles. Some contractors use several fine and coarse aggregates to compose a mix at optimum cost. Coarse aggregates have a maximum size larger than 1/4 inch. Fine aggregates are equal to or smaller than 1/4 inch. Gradation is the distribution of sizes as a percentage of the total weight of the aggregates.

Standardized sieves are used to measure the gradation of a combined aggregate. The aggregate is shaken through a stack of sieves in which the top one has the largest opening and the bottom one has the smallest. The aggregate left on each sieve is weighed and its percentage is calculated or plotted on a standard gradation chart (c.f. Fig. 4)

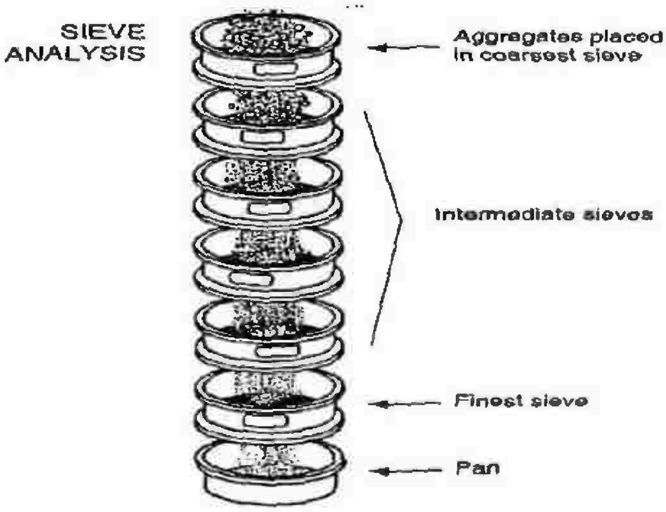


Figure 4: Determining the size and gradation of aggregates

Toughness measures aggregate strength and resistance to polishing and breaking. It is measured by tumbling aggregate in a drum with steel balls. The amount lost when the aggregate is sieved on a specific sieve size is an indicator of toughness or resistance to abrasion.

Surface texture of aggregate influences its workability and the strength of the asphalt mixtures. A rough, sandpaper- like surface texture tends to increase strength more than a smooth surface. It requires more asphalt for the same workability.

Shape is important because it changes the workability and strength of asphalt mixtures. Irregular and angular particles, like crushed stone and gravel, tend to interlock more when compacted and therefore to resist displacement. An indicator of angularity is the percentage by weight of aggregates with one or more fractured surfaces. Absorption is important because highly absorptive aggregate soaks a significant amount of asphalt into its pores, leaving too little to coat and lubricate the mix.

Affinity to asphalt is important particularly when pavements are subjected to high moisture. Aggregates with low affinity to asphalt lose their asphalt cover rapidly when it is stripped by water. Using hydrophilic or water loving aggregates, like quartzite and some granites, can result in major pavement failures when used in wet areas.

Marshall Test for Hot Mixtures [58]:

The design of asphalt paving mixes by using Marshall Test is used as a guide for expected performance characteristics asphalt/ aggregate mixtures and also to establish the proper mixture proportions and the asphalt content that yields a mix haring.

a- Sufficient asphalt to insure a durable pavement by coating thoroughly the aggregate particles and water proofing and bonding them together under suitable compaction.

b- Sufficient mix stability to satisfy the service requirement and demands of traffic without diction or displacement.

c- Sufficient voids in the total compacted mix to provide a reservoir of space to a slight amount of additional compaction under traffic loading to avoid flushing and loss of stability.

d- Sufficient workability to permit an efficient construction operation in the placement of the paving mix.

Measurement of "Marshall Test":

The measurements of Marshall Test are:

1-Stability which is defined as the maximum load resistance to deformation, and can be considered as the loaded or stress to cause a certain amount of deformation or strain.

2- Resistance to plastic flow which is defined as total movement or strain occurring in the specimen between no loaded and maximum load during the stability test.

3- Bulk specific gravity of compacted mixture. The Marshall stability and flow numbers are qualitative measures of a pavement's ability to withstand traffic load and permanent deformation, respectively.

Saad Abo-Qudais et al [59] illustrated the number of cycles that cause fracture of hot-mix asphalt (HMA) based on the number of cycles at which the slope of accumulated strain switched from decreasing to increasing mode. In addition, the effect of aggregate gradation and temperature on fatigue behaviors of HMA was evaluated. HMA specimens were prepared at optimum asphalt content using the Marshall mix design procedure. The specimens were prepared using crushed limestone aggregate, 60/70 penetration asphalt, and three different aggregate gradations with maximum nominal aggregate size of 12.5, 19.0, and 25.0 mm. Five magnitudes of load (1.5, 2.0, 2.5, 3.0, and 3.5 kN) were evaluated for their effect on fatigue behavior. Constant stress fatigue tests were performed using the Universal Testing Machine (UTM) at 25 °C. Other temperatures (10, 45, and 60 °C) were evaluated at a load of 3.5 kN. The tests results indicated that the slope of accumulated strain continued to decrease until the number of loading cycles approached 44% of the number of cycles that caused fracture of the HMA. Also, the initial stiffness of asphalt mixtures was found to increase as the magnitude of the load applied increased and as the aggregate gradation maximum nominal size decreased

Hu¨ seyin Akbulut et al [60] illustrated that More than 95% of asphalt pavement materials (by weight) consist of aggregates. The highway and construction industries consume a huge amount of aggregates annually causing considerable energy and environmental losses. The aggregates are usually produced from neighborhood aggregate quarries or from natural aggregate sources. As a result of the increasing demands for new aggregate quarries, the general texture of earth's surface has been steadily deteriorating, causing environmental concerns. The use of marble wastes from marble quarries as aggregates might help meet the increasing demands and slow down any detrimental effects on the environment. In this study, recycled aggregates produced from homogeneous marble and site quarry wastes in Afyonkarahisar–Iscehisar region were compared to two other aggregate specimens currently used in Afyonkarahisar city asphalt pavements. Los Angeles abrasion, aggregate impact value, freezing and thawing, flakiness index and Marshall Stability flow tests were carried out on the aggregate specimens. The test results indicate that the physical properties of the aggregates are within specified limits and these waste materials can potentially be used as aggregates in light to medium trafficked asphalt pavement binder layers.

Mustafa Karas_ahin et al [61] studied the use of marble dust collected during the shaping process of marble blocks has been investigated in the asphalt mixtures as filler material. The samples having marble dust and limestone dust filler were prepared and optimum binder content was then determined by Marshall Test procedure. Dynamic plastic deformation tests were carried out by using the indirect tensile test apparatus. Optimum filler content was then determined considering the filler/bitumen ratio and filler ratio. Test results showed that plastic deformation of marble waste is between the upper and the lower limits of grounded marbles. The study showed that marble wastes, which are in the dust form, could be used as filler material in asphalt mixtures where they are available and the cost of transportation is lower than ordinary filler materials.

P. Ahmedzade et al [62] studied the benefits of adding Tall oil pitch (TOP), Styrene-butadiene-styrene (SBS) and TOP + SBS to AC-10 in variant quantities to AC-10 were investigated. Initial research was done to determine the physical properties of asphalt cement and modifiers. Seven asphalt binder formulations were prepared with 8% of TOP; 8 + 3, 8 + 6 and 8 + 9% of TOP + SBS, respectively; 3, 6 and 9% of SBS by total weight of binder. After that, Marshall Samples were prepared by using the modified and unmodified asphalt binders. Additionally, compression strength test were done in different conditions to determine water, heat and frost resistance of all Marshall Samples. Fatigue life and plastic deformation tests for Marshall Samples (for different asphalt mixtures: modified and unmodified) were carried out using PC controlled repeated load indirect tensile test equipment developed at Suleyman Demirel University by Tigdemir (SDUAsphalt Tester). The results of investigation indicate that asphalt mixture modified by 8% TOP + 6% SBS gives the best results in the tests that were carried out in this study, so that, this modification increases physical and mechanical properties of asphalt binder.

L.E. Cha′ vez-Valencia et al [63] investigated asphalt (A1) of the Marshall specimens tested in the third step of response surface methodology (RSM) and asphalt (A2) of the cores with real aging was recovered. Adherence and hardness of the asphalts (A1 and A2) were tested by a texture analyzer, and also penetration test was evaluated. The crystallised fractions (CF) and the carbonyl groups (CQO) contents of the asphalts (A1 and A2) was determined by differential scanning calorimeter (DSC) and Fourier Transform Infrared (FTIR), respectively. The change in the content of CF and CQO for A1 was described by a first-order Arrhenius equation, with a small activation energies that suggested a diffused–controlled process of the crystallites and the oxidation of the asphalt,which is related with the decrement in adherence and the increment in hardness and in penetration, highly dependent of aging time.

G.D. Airey et al [64] investigated the influence of asphalt mixture type (aggregate gradation) and compaction energy level on the degradation of aggregate during laboratory compaction. The most severe form of laboratory compaction in terms of potential aggregate degradation, i.e. Marshall (impact) compaction has been used together with a standard UK aggregate and two asphalt mixture gradations consisting of a continuous and gap-graded mixture design. The results of aggregate degradation have been determined by comparing the aggregate gradation in terms of retained aggregate per individual sieve size before and after compaction. The aggregate gradation after compaction has been determined by recovering the aggregate from compacted asphalt mixture specimens and then re-grading using the series of sieve sizes used to batch the original material. The results show that asphalt mixture type and therefore aggregate gradation has a far greater influence on aggregate degradation under compaction than alterations to the level of compaction energy within the normal compaction levels experienced in the laboratory. The gap-graded asphalt mixture experienced a greater amount of aggregate degradation after compaction compared to the continuously graded mixture. The effect of increased compaction energy level did not alter the pattern of aggregate degradation for the continuously graded asphalt mixture and only increased the degree of degradation by a small amount.

Perviz Ahmedzade et al [65] illustrated The properties of AC-5 control asphalt binder, mixture containing the same asphalt were compared with the properties of AC-10 asphalt binder modified by 0.75%, 1%, 2%, and 3% of polyester resin (PR), mixture containing pure AC-10 and AC-10 modified by 0.75% of PR, respectively. Initial research was done to determine the physical properties of unmodified and PR modified asphalt binders. The AC-10 asphalt binder modified by 0.75% of PR had good results compared to AC-5 control asphalt binder and all other modified binders, and hence this modified binder as well as unmodified binders were used to prepare Marshall samples for Marshall stability and flow, indirect tensile stiffness modulus (ITSM), indirect tensile strength (ITS) and creep stiffness tests. The results of investigation indicate that AC-10 + 0.75% PR binder has better physical properties than AC-5 control asphalt binder and, at the same time, PR improves mechanical properties of asphalt mixture.

Saad Abo-Qudais [66] showed that the main objective of his study was to investigate the effects of evaluation methods on the prediction of environmental damage (stripping) of hot mix asphalt (HMA). To achieve this objective, four different environmental damage evaluation techniques were used to evaluate asphalt mixtures prepared using different mix parameters. The environmental damage evaluation techniques include either percent reduction in indirect tensile strength or Marshall Stability or percent increase in static creep deformation due to environmental damage. In addition, the Texas boiling test which is based on visual evaluation of the percent of coated aggregate was used for environmental damage evaluation. The findings of this study indicated that the estimated environmental damage is significantly affected by the method of evaluation. Retained indirect tensile strength and retained stability were found to be less sensitive to environmental damage. Moreover, the static creep test was the only method used that was able to monitor the effect of used asphalt and aggregate gradation on the environmental damage of HMA, while the effect of anti-stripping additives on reduction stripping was easily monitored by the Texas boiling and static creep test. Finally, it was found that different environmental damage evaluation techniques revealed different results of using calcium stearate hydroxide.

Ibrahim M. Asi [(67)] showed that at all stages of pavement life, the highway surface should have some sort of roughness to facilitate friction between car wheels and pavement surface. Skid resistance is a measure of the resistance of pavement surface to sliding or skidding of the vehicle. It is a relationship between the vertical force and the horizontal force developed as a tire slides along the pavement surface. The texture of the pavement surface and its ability to resist the polishing effect of traffic is of prime importance in providing skidding resistance. Polishing of the aggregate is the reduction in micro texture, resulting in the smoothing and rounding of exposed aggregates. This process is caused by particle wear on a microscopic scale. It is a common fact that the lower the skid resistance value, the higher the percentage of the traffic accidents, especially during the wet seasons. Having a low skid resistance value at an asphalt concrete surface might be attributed to one or more of the following reasons: (1) use of higher asphalt content than recommended by the mix design procedure, (2) the Marshall Mix design procedure itself, (3) used aggregate gradation, and (4) aggregate quality. To evaluate these factors, a comparative study was performed to find the British Pendulum Skid Resistance Number for a number of mixes. These mixes included, an asphalt concrete mix using local aggregate at the optimum Marshall asphalt content, mixes with 0.5% and 1.0% asphalt contents higher than Marshall optimum asphalt content, a mix designed using Super pave design procedure, a mix with steel slag to replace 30% of limestone aggregate, and a mix with stone matrix aggregate gradation. It was found that the mix with 30% slag has the highest skid number followed by Super pave, SMA, and Marshall mixes, respectively. It was also observed that increasing the asphalt content above the optimal asphalt content value decreases the skid resistance of these mixes.

Yiik Diew Wong et al [(68)] illustrated the feasibility of partial substitution of granite aggregate in hot-mix asphalt (HMA) with waste concrete aggregate was investigated. Three hybrid HMA mixes incorporating substitutions of granite fillers/fines with 6%, 45% untreated, and 45% heat-treated concrete were evaluated by the Marshall mix design method; the optimum binder contents were found to be 5.3%, 6.5% and 7.0% of grade Pen 60/70 bitumen, respectively. All three hybrid mixes satisfied the Marshall criteria of the Singapore Land Transport Authority (LTA) W3B wearing course specification. The hybrid mix with 6% concrete fillers gave comparable resilient modulus and creep resistance as the conventional W3B mix, while hybrid mixes with higher concrete substitutions achieved better performance. X-ray diffraction (XRD) showed the distinct presence of free lime in the heat-treated concrete, while the scanning electron microscope

(SEM) provided an in-depth perspective of the concrete grains in the HMA matrix. The results suggest feasible use of waste concrete as partial aggregate substitution in HMA

Ibrahim M. Asi [69] investigated a stone matrix asphalt (SMA) is a hot mixture asphalt consisting of a coarse aggregate skeleton and a high binder content mortar. It was developed in Germany during the mid-1960s and it has been used in Europe for more than 20 years to provide better rutting resistance and to resist studded type wear. The main objective of this research study was to compare the performance of the normally used dense graded asphalt mixtures, named in this research as control mixtures, and SMA mixtures. Samples from both mixtures were fabricated at their optimum asphalt contents that were 5.3% for control mixtures and 6.9% for SMA mixtures. Comparison performance tests that included Marshall Stability, loss of Marshall Stability, split tensile strength, loss of split tensile strength, resilient modulus, fatigue, and rutting testing were performed on both mixtures. Test results showed that although the control mixtures have higher compressive and tensile strengths, SMA mixtures have higher durability and resilience properties. In addition, although the research could not prove the superiority of SMA in rutting resistance because of the limited sample sizes, field performance of SMA mixtures proves its superiority. Therefore, especially in hot weather climates, these properties, (durability, resilience and rutting resistance) give SMA mixtures advantages over dense graded mixtures.

Chin-Ming Huang et al [12] studied the results from a research project sponsored by Taiwan Environmental Protection Administration (TEPA), investigating both the physical and environmental properties of asphalt mixtures using different amounts of incinerator bottom ash (IBA) as fine aggregate substitution. The Marshall Mix design method was used to determine the design asphalt content and evaluate the potential performance of these IBA–asphalt mixtures. Water sensitivity and wheel track rutting were also performed on these mixtures. Leachates, from both laboratory and outdoor leaching tests, were performed to measure the concentration of selected heavy metals and the level of daphnia toxicity. While with adequate Marshall Stability, the IBA–asphalt mixtures were shown to have excessively high Marshall flow and excessively low VMA (voids in the mineral aggregate). The results of the wheel tracking tests also indicated that the IBA–asphalt mixtures had low rutting resistance. The results of the water sensitivity test according to procedure of AASHTO T283 method showed that the IBA–asphalt mixtures had a higher tensile strength ratio (TSR) as compared with the conventional asphalt mixtures. Considering the environmental aspects, outdoor leaching tests showed that IBA had a high level of daphnia toxicity. From an ecological perspective, IBA could be identified as hazardous waste in Taiwan. However, after being mixed with asphalt binder, the concentration of heavy metals and the levels of daphnia toxicity were significantly reduced. The leachates of 10-day flat plate leaching tests on Marshall Specimens containing IBA indicated that the heavy metal was undetectable and the daphnia toxicity was ineffective.

Ibrahim M. Asi (71) studied the empirical nature and the drawbacks of the Marshall mix design procedure, the Strategic Highway Research Program (SHRP) has developed a Superior Performance asphalt Pavements (SUPERPAVE) mix design procedure. In this research a comprehensive evaluation of the locally available aggregate usually used in the asphalt concrete mixtures was carried out to ensure that these materials conform to the new mix design procedures developed by SUPERPAVE. A performance grading map was generated to the Hashemite Kingdom of Jordan. In this map the country was divided into different zones according to the highest and lowest temperature ranges that the asphalt might be subjected to. Using local materials, loading and environmental conditions, a comparative study of the performance of two mixes designed using SUPERPAVE and Marshall Mix design procedures was carried out in this research. Samples from both mixes were prepared at the design asphalt contents and aggregate gradations and were subjected to a comprehensive mechanical evaluation testing. These tests included Marshall Stability, Loss of Marshall Stability, Indirect Tensile Strength, Loss of Indirect Tensile Strength, Resilient Modulus, Fatigue Life, Rutting, and Creep. In all the performed tests SUPERPAVE mixes proved their superiority over Marshall Mixes. Therefore, serious plans should be set up in Jordan to shift from the presently used Marshall Mix design procedure to SUPERPAVE mixture specifications.

Ahmet Tortum et al [72] inestigated the Taguchi method was used to determine optimum conditions for tire rubber in asphalt concrete with Marshall Test. The tire rubber in asphalt concrete was explored under different experimental parameters including tire rubber gradation (sieve #10–40), mixing temperature (155–175 °C), aggregate gradation (grad. 1–3), tire rubber ratio (0–10% by weight of asphalt), binder ratio (4–7% by weight of asphalt), compaction temperature (110–135 °C), and mixing time (5–30 min). The optimum conditions were obtained for tire rubber gradation (sieve #40), mixing temperature (155 °C), aggregate gradation (grad. 1), tire rubber ratio (10%), binder ratio (5.5%), compaction temperature (135 °C), mixing time (15 min).

Burak Sengoz, and Ali Topal [73] evaluated like other construction materials, shingles have their own service life based on raw materials, production method and environmental and climatic conditions. At the end of their service life, shingles need to be replaced. However, these old shingles together with manufacturing scrap and handling waste require large storage areas and pollute the environment in time. Hence, additional usage of shingle waste is desirable. In this study, shingle waste in amounts of 1%, 2%, 3%, 4% and 5% by weight was added as an additive to asphalt concrete mixes prepared with the optimum binder content which yielded the best stability value was 5%. After determination of the optimum percentage of shingle to be added, rutting tests were performed on the specimens. Taking into account, the binder content existing in the shingle, mixtures were prepared with the reduced binder content by 0.5% and 1.0%. Test results show that waste shingles can be used in HMA as an additive to improve the Marshall stability and rutting resistance of the mixtures.

Der-Hsien Shen et al [74] investigated the aggregate of natural crush stone in hot mix asphalt is applied to gap gradation mixed with the AC-20 binder, in accordance with Marshall mix design. Laboratory tests were conducted, and the single-factor variance analysis (ANOVA) is employed to estimate the significance of the gradation mixture properties. Based on permanent deformation tests and analytical results, sieve of 2.36 mm may be omitted for nominal maximum aggregate size (NMAS) of 12.5 mm, and sieve of 4.75 mm may be omitted for NMAS of 19 mm, in the case of the shortage of aggregate.

Atakan Aksoy et al [75] illustrated that the effects of four additives, namely two fatty amine (Wetfix I, Lilamin VP 75P), one catalyst

(Chemcrete) and a polymer (rubber), on the moisture damage of asphalt mixtures were studied. Rheological characteristics of the binders were measured using conventional methods both original and thin-film oven aged. Mechanical characteristics of the mixtures were evaluated with Marshall, indirect tensile and Lottman treatment tests. The additives used in this study reduced the level of damage due to moisture in asphalt mixtures. Minimum acceptable indirect tensile strength ratio (0.70) is achieved when Chemcrete and 0.2% of Wetfix I, and 0.4–0.6% of Lilamin VP 75P are used in asphalt mixtures. Indirect tensile strength ratio may decrease due to the relatively higher strength obtained in dry specimens with respect to the conditioned ones. Indirect tensile strength ratios of asphalt paving specimens were found to be less than the Marshall Stability ratios.

Sinan Hınıslıog, Emine Ag [(76)] illustrated that the purpose of his study is to investigate the possibility of using various plastic wastes containing High Density Polyethylene as polymer additives to asphalt concrete. It was investigated that the influence of HDPE-modified binder obtained by various mixing time, mixing temperature and HDPE content on the Marshall Stability, flow and Marshall Quotient (Stability to flow ratio). The binders used in Hot Mix Asphalt (HMA) were prepared by mixing the HDPE in 4–6% and 8% (by the weight of optimum bitumen content) and AC-20 at temperatures of 145–155 and 165 °C and 5–15 and 30 min of mixing time. HDPE-modified asphalt concrete results in a considerable increase in the Marshall Stability (strength) value and a Marshall Quotient value (resistance to deformation). Four percent HDPE, 165°C of mixing temperature and 30 min of mixing time were determined as optimum conditions for Marshall Stability, flow and Marshall Quotient (MQ). MQ increased 50% compared to control mix. It can be said that waste HDPE-modified bituminous binders provide better resistance against permanent deformations due to their high stability and high Marshall Quotient and it contributes to recirculation of plastic wastes as well as to protection of the environment.

Nan Su, J.S. Chen [77] showed that Taiwan is an island nation with high population density: 23 million people living in a total land area of 30 000 sq. km. The island has transformed from an agricultural society to an industrial one in the past three decades. Coming with the transformation is a cumulated waste problem. Taiwan produces nearly 5 million tons of waste each year, of which 10% is of glass materials. Bureau of Highway Department funded a research program to investigate ways of recycling the glass waste. This report presents information on the program and laboratory/field test data. Materials used in the test program included 85/100 asphalt, Type II modified asphalt, and treated glass waste. Four glass contents: 0, 5, 10, and 15%, in terms of the total aggregate weight, were used in the mixture designs for casting series of 10 cm diameter by 6.35 cm disk specimens. Tests including Marshall Stability value, dry/wet moisture damage, skid resistance, light reflection, water permeability, and compaction were carried out in accordance with the ASTM and AASHTO procedures. The test results reveal that glass waste is a viable material for asphalt concrete that has been widely used in pavement that offers profound engineering and economic advantages.

Ziauddin A. KhanU et al [78] explained that the main objective of his study was to compare different laboratory compaction methods to field compaction and to select the laboratory method that was similar or close in compaction to that of the field. The candidate compaction methods were: a. Marshall Automatic Impact Compaction; b. Marshall Manual Impact Compaction; California Kneading Compaction; d. Gyratory Shear Compaction angle of gyration 1.258. Gyratory Shear Compaction - angle of gyration 68. The evaluation m of the five laboratory compaction methods was based on the similarity between the engineering properties of the laboratory compacted samples and the field cores. The engineering properties studied were resilient modulus, air voids, bulk density, and static creep behavior. The laboratory compacted specimens and field cores were also evaluated with the objective of identifying a promising laboratory compaction technique which would be able to produce mixtures with engineering properties closest to those of mixtures compacted in the field. Samples for this study were selected from four projects located at different locations in the Eastern Province of Saudi Arabia. The principal conclusion of the study was that the Gyratory Shear Compaction _angle of gyration 1.258. Method best represented the engineering properties of the field cores.

Kwang W. Kim et al [79] investigated the possibility of utilizing a polyester resin for reinforcing flexible pavements. The application of a thin-layer coating with a polymer, unsaturated polyester resin (UPR) on the surface of a laboratory-prepared unmodified asphalt concrete mixture was studied as a tensile reinforcement method for such a material. Selected laboratory performance tests were conducted and the results are compared with those of a normal (uncoated) asphalt concrete mixture and a modified asphalt mixture, both mixtures being widely used in Korea. The polymer coating was found to be effective in improving Marshall Stability, tensile strength and flexural strength of asphalt concrete. These improvements can be explained as the effect of reinforcement by a thin polymer layer which is fully bonded to the specimen faces.

The reinforcement was also effective in reducing the stiffness of the mixture whilst improving load-carrying capacity. This improvement in strength and reduction in stiffness resulted in a retardation of crack initiation resulting from cyclic load application and a significantly improved resistance to crack propagation. The study has shown that there is a possibility of using the polymer coating as a method of tensile reinforcement with flexible pavements.

Masahiro Kouda (80) showed that municipal wastes used to be simply land filled, but because of increasing difficulty in finding disposal sites, it became common practice to incinerate wastes and landfill the ash. In view of rapidly dwindling landfill sites, the author thought that the landfill site problem might be solved by finding a way to utilize slag made from incinerator ash. In this paper, a method for utilizing water-granulated slag as an asphalt pavement material is discussed. On the basis of laboratory test results, trial paving using base course materials consisting of crushed stone and 25 or 50% slag was carried out, paying attention primarily to bearing capacity. Marshall tests and fatigue resistance tests were conducted to determine the optimum content of water-granulated slag, and it was concluded that quality comparable to that of conventional asphalt concrete was attained at the slag content of 25% or less and that no problem would arise if the slag content was kept at 60% or less of the fine aggregate content. The mix proportions thus determined were also tested through experimental paving. A follow-up study to evaluate the durability of the experimental pavements confirmed that the experimental pavements were comparable in performance with conventional asphalt concrete pavements. This paper also reports on some problems encountered that need to be solved before utilizing water-granulated slag.

Nanomaterial and Nanotechnology

Nanocomposites have received much attention in the industry and academia due to the enhanced thermal properties, mechanical properties, etc., for a few weight percent of inorganic filler content dispersed within organic matrix at a nano-scale in comparison with a micro-scale for conventional composites[81].

Nanomaterial and nanotechnology are the science and engineering of creating materials, functional structures, and devices on a nanometer scale. In scientific terminology "nano" means 10^{-9}:

Nano-structured inorganic, organic, and biological materials may have existed in nature since the evolution of life on earth. Some evident examples are microorganisms, fine-grained minerals in rocks, nano-particles in bacteria

Why are we so fascinated with downsizing materials to a nano-scale?

The fundamental physical, chemical, and biological properties of materials are surprisingly altered as their constituent grains are decreased to a nanometer scale owing to their size, shape, surface chemistry, and topology. For example, 6 nm copper grains show five times more hardness than conventional copper. Cadmium selenide (CdSe) can be made to yield any color in the spectrum simply by controlling the size of its constituent grains[82].

There are several major government programs on research and development of nano-structured materials and nanotechnology in the United States, Europe and Asia.

Recently, in Egypt, the first national conference of scientific research (EGYPT, FUTURE), which held in 28-29 May 2005, Cairo, considered that the nano-materials and nano-technology is one of the priorities of Egyptian scientific research.

Method of preparation:-

A) Bottom Up B) Top down

Bottom up

Means starting with atom or molecules and build them up from the final nanocrystalline form. There are six common methods for preparation nanostructure materials.

1- Co precipitation Method

It is the most common method; it allows the precipitation of the starting cations from solutions under continues flow of the hydroxid ions at high temperature and vigorous stirring.

The idea of the co precipitation method is the idea of nanotechnology: allowing only small number of atoms or molecules to be collected together to form the crystal or the particle or the grain of the final precipitate, so, the need of high temperature and vigorous stirring (work against the precipitation of the cations simultaneously by the action of the gravity).

2- The hydrothermal method:

Exactly as the co precipitation method, but with the use of autoclave to ensure maximum stirring and high temperature (preferred, reduces the aging time, and reflects the important of high t with stirring), it provides a sharp crystalline nanostructures.

3-sol- gel method

It is the simplest method, it involves insitu precipitation of the starting cations from their mother solution by using high temperature dissociating organometalic components in presence of buffer under vigorous stirring, here the separation of the metal cation from the organometalic compound occurs slowly and reacts with the minimum number of the hydroxide part.

4- Electrodeposition method:

It is similar to the electroplating method to far extend (depends on faradays law of electricity), the only deference is that, controlling the number of passing electrons that allow precipitation of the cations and also applying very dilute solutions with aid of as large as possible electrodes.

5- Chemical vapor deposition

It involves evaporation of the starting material to the gas phase (without ionization) by electrical or thermal heat under vacuum (if the oxide or carbide forms are not wanted) allowing the vapor to pass through a very narrow frit to condense on a very large surface (remember the idea of nanotechnology is how to allow only small number of atoms or molecules to be collected during the formation of the crystal or the grain of your object matter).

6- Plasma arcing

Plasma is the fourth state of matter and it means presence of the matter in ionized gas phase. In this method, the starting material is applied as electrode under vacuum and a potential difference, the electrode starts to vapors and ionize then allowed to be neutralized and deposited on a large surface

Top down methods

In most are mechanical or engineering methods. Means: starting with the large object or material and break it down under sever conditions to form the nanocrystalline form.

Ball milling

Mechanical crushing method for the preparation of nanostructure. It involves insertion of starting materials between two or more balls in a drum, the balls are allowed to rotate and fall down by the action of gravity, and this leads to breaking of the structure into the nanostructure.

Laser ablation

Applying the laser technique to screen, photograpf and magnify the surface of the starting material, so, can control the number of sheets or layers accurately then bombarding the distance between the choosed number of sheets with the laser bulses leads to the ablation of the minimum layers of the material that consists of small number of atoms or molecules or thin films crystal.

Using Atomizer Technique

A high electrical field is used to atomize the starting material and then allow the smallest number of atoms to be collected to form the final nanocrystal object.

Clay has been used as a natural rubber filler for many years but the reinforcing ability of clay is poor due to its large particle size and low surface activity. Many researchers have succeeded in intercalating various polymer in the clay interlayer to prepare clay/polymer nanocomposites [83].

The first such clay-based nanocomposites were synthesized by a Toyota research group using a polyamide as the polymer matrix. The work was expanded with various polymers and these include polypropylene, ethylene–propylene–diene monomer (EPDM), styrene, poly(methyl methacrylate), ethylene vinyl acetate, and many others [83, 84].

The nanocomposites showed major improvements in physical and mechanical properties, heat stability, reduced flammability and provide enhanced barrier properties at low clay contents [83].

Study of synthetic rubber and natural rubber/clay composites cured by sulfur or peroxide have been carried out by several researchers. Okada et al. [83] showed for acrylonitrile butadiene rubber (NBR) cured by sulfur that only 10 phr organoclay were necessary to achieve tensile strength comparable to compounds loaded with 40 phr carbon black.
Jamaliah Sharif et al [83] illustrated that radiation crosslinking of natural rubber (NR)/clay anocomposites was studied by using Standard Malaysian Rubber (SMRL) grade natural rubber and sodium montmorillonite (Na-MMT) clay that had been modified with cationic surfactants, dodecyl ammonium chloride (DDA) and octadecylamine ammonium chloride (ODA). The NR/clay nanocomposites were prepared by melt mixing to produce NR/Na-MMT, NR/DDA-MMT and NR/ODA-MMT composites. X-ray diffraction results indicated the intercalation of the NR into silicate nano-size inter-layers for NR/DDA-MMT and NR/ODA-MMT nanocomposites. An optimum electron beam dose of 250 kGy for crosslinking of NR, NR/DDA-MMT and NR/ODA-MMT was determined by gel content and tensile strength measurements. Upon electron beam irradiation, the tensile modulus of the nanocomposites keeps increasing with the increase of clay content

up to 10 phr. However, the tensile strength and gel content of the nanocomposites show optimum values at a range of 3.0–5.0 phr clay content. From these results, NR/DDA-MMT shows higher tensile strength, whereas NR/ODA-MMT exhibits higher tensile modulus. The optimum tensile strengths of NR/DDAMMT and NR/ODA-MMT are 12.1 and 9.5 MPa, respectively. TGA studies showed that NR/DDA-MMT and NR/ODA-MMT nanocomposites have higher decomposition temperatures in comparison with the NR/Na-MMT.

Y. Xiang et al [85] investigated a new type of stimuli-responsive organic/inorganic nano-composite hydrogel was prepared by introducing fibrillar attapulgite into poly(2-hydroxyethyl methacrylate-co-poly(ethylene glycol) methyl ether methacrylate-co-methacrylic acid) network, in which the nanosized attapulgite fibril worked as the cross-linker instead of conventional chemical cross-linker. In the preparation process, a prepolymerization route was adopted to effectively stabilize the dispersion of attapulgite. The structure and morphology of the nano-composite hydrogels were characterized by SEM, FTIR and DSC. The swelling/deswelling behaviors and tensile mechanical properties of the nano-composite hydrogels were compared with that of the corresponding chemically cross-linked hydrogel. The results showed that the nano-composite hydrogels had much greater equilibrium-swelling ratio, much faster response rate to pH and significantly improved tensile mechanical properties. As the content of AT increased, the tensile strength, effective cross-link chain density and glass transition temperature increased, while the equilibrium swelling ratio, deswelling rate and elongation at break decreased.

S. Balakrishnan et al [86] showed that the influence of toughener and clay concentration on the morphology and mechanical properties of three-phase, rubber-modified epoxy nanocomposites was studied. Nanocomposite samples were prepared by adding octadecyl ammonium ion exchanged clay to a dispersion of preformed acrylic rubber particles in liquid epoxy, so as to minimize alteration to the rubber morphology in the final cured specimen. The state of clay platelet exfoliation and rubber dispersion in the cured nanocomposites was studied using transmission electron microscopy. The amounts of clay platelet separation and dispersion of clay aggregates in the epoxy matrix were found to be sensitive to clay and toughener concentration, and clay platelets preferentially adsorb to the rubber particles. Tensile modulus and strength increase and ductility decreases with increasing organoclay content, while rubber has the opposite effects on the properties of epoxy resin. When both additives are present in epoxy resin, a favorable combination is produced: ductility is enhanced without compromising modulus and strength. Modulus and strength are improved by nano and micro dispersion of nanoclay in the epoxy matrix, whereas elongation and toughness are improved by clay adsorption to the rubber particle surface, which promotes cavitation. The glass transition temperature of epoxy resin remains relatively unchanged with clay addition.

You-Ping Wu [87] investigated that the structure of several rubber–clay nanocomposites, including styrene butadiene rubber (SBR)–clay, natural rubber (NR)–clay, nitrile butadiene rubber (NBR)–clay, carboxylated acrylonitrile butadiene rubber (CNBR)–clay nanocomposites, prepared by directly co-coagulating the rubber latex and clay aqueous suspension, were investigated. X-ray diffraction (XRD) patterns and transmission electron microscopy (TEM) micrographs showed that these nanocomposites possessed a unique structure, in which the rubber molecules "separated" the clay particles into either individual layers or just silicate layer aggregates of nanometer thickness without the intercalation of rubber molecules into clay galleries, different from intercalated and exfoliated clay nanocomposites. Such a structure resulted from the competition between separation of rubber latex particles and re-aggregation of single silicate layers during the co-coagulating process. The content of bound rubber of SBR–clay nanocompound is more than that of the corresponding rubber filled with micrometer clay or silica because of the increased networking of silicate layers with the nano-meter dispersion and the high aspect ratio. The glass transition temperature of SBR–clay nanocomposites increased as compared with that of the pure SBR. The tensile strength of SBR–clay nanocomposite loading 20 phr clay was 6.0 times higher than that of the conventional SBR–clay composite. The gas permeability of separated rubber–clay nanocomposites containing 20 phr decreased 50% as compared with the corresponding gum vulcanizates.

A.J. Brunner et al [(88)] illustrated that dispersion of nano-sized, silicate-based filler in epoxy resin is expected to yield improved materials properties in several areas. Various mechanical properties, specifically improved fracture toughness, as well as improved flame-retardant effects are of interest. The final objective of the research is investigating whether a nano-modified epoxy matrix yields improved delamination resistance in a fiber-reinforced laminate compared to a laminate with neat epoxy as matrix material. As a first step towards this goal, the fracture toughness of nano-modified epoxy resin is compared with that of the neat resin. Fracture toughness improvement up to about 50%

and energy release rates increased by about 20% are observed for addition of 10 wt.% of organosilicate clay.

Yuma Konishi, Miko Cakmak[89] investigated that the influence of platelet-type clay nanoparticle (nanoplatelet) on the structural evolution in injection-molded nylon 6)/carbon composites was investigated. In the absence of nanoplatelets, the nylon 6/CB systems were found to exhibit unoriented structure with nylon 6 crystalline regions exhibiting exclusively a crystal form throughout the thickness of the samples. However, inclusion of nanoplatelets induces substantial local orientation of the nylon 6 chains in the molded parts in all processing conditions and compositions. In these clay/nylon 6/CB ternary nano systems, nylon 6 matrix was found to be exclusively in g crystal form at the skin regions and a crystal form fraction increases towards the core of the molded parts as a result of decrease in cooling rate with depth during the solidification stage. Two nanoplatelet orientation behaviors were identified: (i) in the absence of irregular shaped CB, the nanoplatelets align parallel with one another following the local flow patterns. The latter behavior also causes enhanced orientation of the nylon 6 chains undergoing substantial shear amplification trapped in between the nanoplatelets (ii) in the CB-enriched regions, nanoplatelets though still remaining parallel to one another, are randomized by following the local contours of irregular shaped CB aggregates. These CB aggregates themselves were found to organize to form trains in larger scale as a result of flow alignment.

Joung Gul Ryu Et al [90] showed that polymer–clay nanocomposites of various concentrations were prepared by ultrasonically assisted polymerization and melt mixing processes. The sonication process using power ultrasonic wave was employed to enhance nano-scale dispersion during melt mixing of monomer, polymer and organically modified clay. According to the unique mode of power ultrasound wave, we expected enhanced breakup of layered silicate bundle and further reduction in the size of dispersed phase with better homogeneity compared to the in situ polymerization. The optimum conditions to perform stable exfoliated nanocomposites were studied by various compositions andconditions. Dispersion characteristics and morphology of the nanocomposites were verified by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Rheological behaviors were measured under dynamic frequency sweep mode using Rheometric science ARES.