Chapter 1

INTRODUCTION
I.1 GENERAL

The history of Petroleum goes back to many centuries before Christ. The Old Testament contains a number of references to large oil and gas seepages and its uses. Noah preparing the arc for the flood, seems to have been one of the first men to have realised the value of petroleum. He used it to calk the seams of his primitive vessel. But even before Noah, prehistoric man undoubtedly had seen, smelled and tasted this strange blackish-green substance.

According to the available evidence, ancient people knew more about asphalt than other forms of petroleum. In the Bible there are references to "Slime" and "Pitch" - ie bitumen or asphalt, the substance left after the gases and liquids of crude oil have evaporated. The basket in which Moses floated in the Nile was water-proofed with asphalt. Arabic literature has references to "eternal fires" presumably caused by natural gas escaping from the earth. For a time ancient man probably had feared it too; strokes of lightening occasionally ignited escaping jets of gas and started fires that in some instances burned for centuries. Precisely when and to what degree ancient man first began to grasp the potential of petroleum is still matters for archeological investigation; but by 4000 B.C. when the
Sumerians were beginning to keep records, it had already been put to use. The Sumerians and later Assyrians and Babylonians used natural asphalt to attach blades to handles of their knives and tools, treat the sick and as mortar for their buildings. These civilizations grouped on the banks of the river Euphrates in what is now Iraq, obtained their asphalt from the "Fountains of pitch" in Hit, about a hundred miles west of Baghdad, where large seepages of petroleum existed.

There are numerous early references to "Neft" (an old Persian word for petroleum from which the English "Naphta" is derived) and to "burning waters". And in the 5th century B.C. the Greek historian Herodatus described how both bitumen and oil were obtained. For many centuries, the recorded uses of petroleum were to destroy enemies in their wars. It was a key weapon in Byzantium's defence when Arab fleets attacked Constantinople in the 7th and 8th centuries.

During the 19th century the development of machines and factories created a large demand for lubricants and lighting oils. Mutton and beef tallow and Castor oil served as lubricants. The demand for lubricants and lamp oil gave rise to a whaling industry so successful that whales were almost exterminated. In 1850 a process to produce oil from coal was patented by Abraham Genser.
In 1855 Samuel Kier built a distillation system in Pittsburg to produce "Carbon oil". This was North America's first oil refinery. Larger demand led to better methods of obtaining petroleum rather than skimming off from the surface of "oil springs". In 1857 a fifty foot well was digged in Canada. In August 1859 an oil well was made by Drake by drilling an iron pipe 70 foot long in Pennsylvania. The well produced upto 35 barrels a day and launched the Petroleum industry as it is known today.

1.2. VARIETIES OF PETROLEUM

Petroleum as it occurs in different parts of the world varies widely in composition. Certain varieties are composed of open chain hydrocarbons. Others are made up exclusively of cyclic hydrocarbons, and still others occur, showing every possible gradation between these two extremes. Numerous classifications have been proposed based on its chemical composition in general, or the presence of a substantial proportion of characteristic bodies, such as paraffin series of Hydrocarbons, the Naphthene series, sulphur derivatives, nitrogenous bodies, benzols, Terprenes etc.

From the standpoint of asphalt content petroleums are divided into three groups:

(1) Asphaltic petroleums: These carry a substantial
quantity of asphaltic bodies with solid paraffins either absent or present only in traces.

(2) Semi-asphaltic petroleums: These carry a moderate quantity of asphaltic bodies, but in any event generate or produce asphaltic bodies during the distillation process. Solid paraffins may or may not be present.

(3) Non-asphaltic petroleums: These do not carry asphaltic bodies but may generate them during the distillation process. Solid paraffins are usually present, but not necessarily so. Asphalt is manufactured from asphaltic and semi-asphaltic crude oils.

1.3. MANUFACTURE OF PAVING BITUMEN

1.3 (a) STRAIGHT REDUCTION FROM CRUDE OIL

Crude oils were originally refined by distillation using batch stills. In the stills, large amounts of steam aided the vapourisation or distillation of the more volatile constituents. When asphalt base crudes were thus processed, the resulting residuum became known as steam reduced asphalt\textsuperscript{5,6}. With the advent of more efficient means of distillation, the terms straight-run asphalt and straight reduced asphalt became more commonly used. These terms imply that the asphalt is separated in such a way as to preserve its inherent properties\textsuperscript{7} ie. by not being affected by cracking or oxidation as occurs in other processes.
Distillation is an integral process in crude oil refining. The initial step in distillation is under atmospheric pressure and normally involves heating the crude oil to about 375°C through a tube heater or furnace, followed by injection into a fractionating column. The lighter fractions are in this way separated as over-head products and the asphalt as a residuum. Use of steam in the distillation tower provides for lower vapour pressures of the distillate fractions, permitting the use of lower temperatures. This results in better operation, economy and the use of higher temperatures without cracking. When the distillation is operated under atmospheric pressures, the asphalt residuum is termed atmospheric residue or topped crude. This becomes the first step in overall refining process.

Many crudes contain relatively high percentages of high boiling fractions which cannot be distilled in an atmospheric distillation unit. In order to obtain residuum of desired asphalt consistancy as well as to recover these high boiling fractions for other purposes, it became necessary to supplement the process. This was done by adding a second fractionating tower, operated under reduced pressure, to permit deeper cutting into the crude. This is the second stage of the distillation process.

The process of manufacturing asphalt by the vacuum
The distillation method has very little effect on the properties of an asphalt, other than on its consistency or penetration. The crude source from which the asphalt is made, does have an appreciable effect on its physical properties. Different crudes also require different process conditions for the separation of an asphalt. This is due primarily to the make-up of the crude, i.e. to the boiling characteristics of the oils present as well as to the quantity of oils to be removed. This is brought out by the relationship of atmospheric cut-point to the yield of the various penetration asphalt residuum. Cut-point as used here is the maximum vapour temperature reached during distillation.

I.3. (b) PROPADE ASPHALTING PROCESS

Asphalt is a by-product of the propane deasphalting and fractionation process[12], which involves the precipitation of asphalt from a residuum stock by treatment with propane under controlled conditions. It has as its primary purpose the recovery of either lube or catalytic cracking stocks. Asphalt manufactured by this process, therefore, is subject to the requirements specified for these oil fractions. Propane is conventionally used in this process although propane-butane mixtures have been used with some variation in processing conditions. Worldwide there are
over 45 propane deasphalting units in operation, mostly on crudes of relatively low asphalt content. These units make asphalt for paving by blending with straight reduced residues.

The process consists of a counter-current liquid-liquid extraction. The charge stock is introduced near the top of an extraction tower and the liquid propane near the bottom using solvent to oil ratios from 3/1 to 8/1. The deasphalted oil solution is withdrawn overhead and, the asphalt solution from the bottom, each being subsequently stripped of propane.

Operating pressures and temperatures are dependant on the proportion of the propane-oil mixture. Temperatures are usually selected to accommodate the charge stock; ie. a temperature must be selected in which the propane-oil mixture has suitable viscosity for fluid handling in the deasphalting tower. High solvent-oil mixtures tend to give high yields of asphalt oil and low yields of asphalt. Operating pressure and temperature are varied depending upon selectivity needed.

Basically there are small differences between asphalts prepared by propane deasphalting and those prepared by vacuum distillation, when processing the same stock. Propane precipitation does have the ability
to reduce a residue further ie, to a harder asphalt product. However, propane deasphalting is conventionally applied to low asphalt content residues which are generally quite different in composition from those processed by vacuum distillation on asphalt bearing crudes. Thus, it is difficult to make comparisons of asphalts prepared by the two processes. However, it is generally observed that for a given softening point we find lower penetrations in the case of the propane precipitation process.

Mixed propane-butane is sometimes used in the deasphalting process. This provides a slightly higher level of flexibility due to higher operating temperature, thus separating an asphalt product of higher softening point and containing a lower percentage of oil. A similar effect is obtained by mixing benzene or other aromatics with either propane or butane. This permits the use of higher temperature and pressures yielding an asphalt approaching 200°C in softening point. Again the effect is to concentrate a higher percentage of asphaltenes in the asphalt product.

1.3.3 DEASPHALTENING PROCESS

In recent years interest has been displayed in deasphalting of residual stocks. This involves the use of solvents such as n-pentane, n-hexane or n-heptane at atmospheric pressure in ratios of 5/1 or greater.
The result is the precipitation of a product that is essentially asphaltenes, thus the term de-asphaltening. The selectivity of this method, in terms of how well the resins and oils are separated from the asphaltenes, depends upon the ability of the process to separate the solid asphaltene product from the solvent-oil-resin solution. Such a separation is usually accomplished by filtration or by centrifuging. As yet, deasphaltening has not been reduced to refinery practice, but it takes little vision to foresee this as an eventuality.

I.4 AIR-BLOWING PROCESS FOR INDUSTRIAL BITUMEN MANUFACTURE

It has been recognised for many years that the physical properties of petroleum products change when treated with air. One of the first to report this fact was Abraham Genser in 1865. Air-blowing is a process in which an asphalt stock is converted at temperatures ranging from 200° to 270°C to a product of modified properties by polymerization in presence of air. This is sometimes called asphalt oxidation with the product termed oxidised asphalt. The terms air-blowing and air-blown asphalt are preferable, however, because it has been shown that dehydrogenation and polymerizations are involved and that oxygen is not added to the asphalt product except in a very minor amount. Naphthene aromatics are converted to polar aromatics and then to asphaltenes. The following
is the scheme of transformations during air blowing of the raw material.

In the beginning of the process

\[ \text{RH} + \text{O}_2 \rightarrow \text{R}^+ + \text{HO}_2^- \]

Interaction of the formed radicals with new molecule of hydrocarbon followed by disproportionation leads to the recovery of stable products.

\[ \text{R}^+ + \text{R}_1^+ \rightarrow \text{RR}_1^+ \]
\[ \text{RR}_1^+ + \text{R}_1^+ \rightarrow \text{RR}_1^+\text{R}_1^+ \rightarrow \text{disproportionation.} \]

As a result of the comparatively low concentration of hydrocarbon radicals, there is less probability of their recombination (\(2\text{R}^+ \rightarrow \text{R}-\text{R}\)) and the interaction of the radicals with oxygen takes place to a smaller extent than with the molecules of the initial substance.

\[ \text{R}^+ + \text{O}_2 \rightarrow \text{ROO}^- \]
\[ \text{ROO}^- + \text{R}_1^+ \rightarrow \text{ROOH} + \text{R}_1^+ \]
\[ \text{ROOH} \rightarrow \text{RO}^- + \text{OH}^- \]
\[ \text{R}_1^+ + \text{OH}^- \rightarrow \text{R}_1^+ \text{H}_2\text{O} \]

Continuation of the chain:

\[ \text{RH} + \text{HO}_2^- \rightarrow \text{R}^+ + \text{H}_2\text{O}_2, \text{H}_2\text{O}_2 \rightarrow \text{2OH} \]
\[ \text{R}_1^+ + \text{OH}^- \rightarrow \text{R}_1^+ + \text{H}_2\text{O} \]
Air-blowing of petroleum residues or fluxes was first patented by Desmedt and first put into commercial practice by Byerley. Originally this was accomplished by injecting air into hot asphalt contained in a horizontal vessel or still. With the development of high pressure blowers it was found that greater efficiency could be realized by using vertical vessels or towers. Other design operating features followed such as the use of agitation and chemical catalysing agents which will be mentioned later. Published literature on air-blowing leaves much to be desired, with no complete treatise on the subject. Perhaps the reason for this problem is that there are many competing reactions involved and with very little published information that may be applied to any particular unit design. The fact that all variables mentioned previously are interdependent plus a general non-uniformity of plant design and practice permits very little opportunity to standardise on methods.

1.4. (a) THE BATCH AIR-BLOWING PROCESS

The batch process for air-blowing is more commonly used than the continuous method. The essential features of the process are

a) a preheat furnace
b) a compressor for air supply
c) a blowing vessel
d) perforated pipes at bottom to subdivide the gas in a fine stream or jet
Preheating is usually accomplished by a tube furnace or heater such as the automatic convective type. Direct fired batch stills or tanks with immersion heaters can also be used to accomplish the same objective. Air supply is commonly provided by compressors of the rotary type. A wide variety of vessels or drums have been adapted to air-blowing of asphalt. Frequently use is made of vessels transferred from other refinery service. Many horizontal type vessels are still in use although where new design is involved, a vertical type is preferable because of better efficiency. Basically the height of asphalt in the blowing vessel is the prime consideration for reasons dependent upon the air supply. If greater capacity is desired, the vessel should be designed with a large diameter. If shorter processing time is desired, the trend would be toward taller vessels of small diameter. The quantity of air is also a factor in the amount of conversion that takes place per unit of time; present day units are designed to operate on 15 to 50 Cu.ft of air per minute per tonne of asphalt charge.

The design of blowing vessels usually includes such features as easily removable air coils to save time in maintenance cleaning, safe and well designed sample ports etc. It has been estimated that exother-
asphalt per degree farenheit of softening point rise. The effect of this exothermic heat is to raise the temperature of asphalt itself. This heat must be removed to some extent to prevent accumulation of very high temperatures which would affect the softening point-penetration relationship of the blown product. Several features have been included in the design to overcome this. One is to provide a pump-around system using a heat exchanger or spraying water directly on the top of the asphalt during blowing.

Air blowing losses will generally vary from ½ to 2% of the charge depending upon the volatility of the flux, temperature, time etc. Process fumes largely account for these losses. The disposal of process fumes has always been a problem with no completely satisfactory answer. These fumes contain hydrocarbons and their derivatives in both vapour and entrained form. The vapours include moisture as well as products from the reaction of air with the asphalt. Such compounds as aldehydes, ketones, sulphur and nitrogen derivatives have been identified in blowing fumes.

The vapourised compounds accounts for the disagreeable odour found in blowing fumes. Entrained oils originate from the asphalt and are representative of the more volatile hydrocarbon constituents in asphalt.
A simple knockout drum or vapour trap in the effluent line following the blowing vessel will do a great deal in deoiling these fumes. The knockout drum is equipped with water sprays which assist in deoiling. Where space is available, a simple system consists of passage of the effluent through a long horizontal air condensor and then into a vertical stack. This will trap out virtually all of the entrained oil and permit better dilution of the vapourised compounds.

**Operation of batch air blowing**

In batch air-blowing, temperature is the most important single variable. Other variables such as air rate, source of flux etc. are generally held constant. Preheating is generally necessary to bring the flux up to a temperature where reaction begins. For practical considerations, this is in the vicinity of 200-270°C; conversion does take place at lower temperature but is very slow. Higher starting temperatures may be used, but it is more practical to use some of the exothermic heat to reach these temperature and thus save input heat. After air has been introduced, there is a gradual temperature rise until some means is applied to hold the temperature of the batch. Water injection is used to control the temperature at a level in the vicinity of 220°C. The end-point can be predicted by testing the batch for softening point periodically. In this way it
is possible to pump out the batch at a predicted time instead of waiting for a final test. As the end point is reached the batch is cooled 20°C or more as quickly as possible. This will aid in maintaining the end-point consistency by preventing depolymerization which frequently occurs when blown asphalts are soaked at high temperatures. This is called quick freezing.

Parameters of the process

1. **Nature of the raw material:**

   Petroleum containing 5% and more by weight of asphaltic-resinous substances are used for the purpose of air-blowing. The best raw materials for obtaining air-blown asphalts are residues of high resinous, low paraffinic petroleums eg; Arab mix, Suez blend, Kuwai
ty, Mexican heavy, Venezuela, Trinidad petroleums etc.,

   The quality of the air-blown asphalt especially the softening point-penetration relationship depends on the nature and consistency of the raw material. For a given softening point, the penetration of the air blown asphalt obtained from the same petroleum depends on the oil content in the raw material. The higher the oil content in the raw material, the higher is the penetration of the resulting air blown asphalt. The air blown asphalts made from propane deasphalted asphalt have higher molecular weights compared to those from vacuum distillation process. The paraffinic petroleums are
not suitable. The paraffin waxes like crystalline substances do not possess the plastic and adhesive properties. The action of paraffinic compounds depends on their dispersion, structure and the permissible content of these compounds in the raw material is upto 3% by weight. The more the paraffinic content in the raw material, the more will be the flow rate of air and oxidation duration.

2. Temperature of the process:

The optimum temperature for air-blowing depends on the nature of the raw material and it is normally between 220 to 240°C. At higher temperatures upto 270°C the rate of increase of softening point increases but results in products of lower penetration for a given softening point. At temperatures above 270°C there is an intensive formation of carbenes and carboids which results in lower penetration and ductility. With rise in temperature, the diffusion constants increase and the surface tension decreases, the size of the gas bubles increase as a result of decrease in the viscosity of the liquid phase, side reactions prevail which do not help in increasing the softening point of the bitumen (Mainly dehydrogenation reactions take place resulting in the formation of carbenes and carboids). Further, at higher temperatures there is an intensive distillation out of lighter fractions. At temperature above 270°C the flow rate of air increases and the
extent of utilization of oxygen of the air decreases.

3. **Flow rate of air:**

The flow rate of compressed air, degree of its dispersion and distribution over the cross section of oxidation tower significantly affect the intensity of the process and the properties of the bitumen. The increase in the flow rate of air up to definite limit, with other conditions being the same, leads to a proportional increase in the oxidation rate; the latter depends on the temperature of the process, construction of the oxidation tower and the nature of the raw material.

The effect of flow rate of air and oxidation duration on the quality of bitumen has not been fully determined. However, it has been found that the bitumens, oxidised in short duration, have higher penetration than the penetration of bitumen of the same softening temperature oxidised in longer duration at lower rate of air supply. This may be explained by the formation of lower molecular polar asphaltenes in the first case. When the duration of oxidation is long and the high temperature acts for a long time, molecules of CO$_2$ split out and the conversion of bitumens into higher molecular weight asphaltenes takes place.

4. **Pressure:**

With increase in pressure in the reaction zone,
the diffusion of oxygen into liquid phase improves, the oxidation duration reduces and as a result of condensation of a portion of oil vapours from the gaseous phase and penetration of the resulting bitumen will be higher. The oxidation under pressure enables the use of raw material with small oil content and produce bitumens having fairly high penetration.

1.4. (b) CONTINUOUS AIR-BLOWING

Continuous air blowing has got certain advantages\textsuperscript{19}, lower equipment and maintenance cost; shorter blowing times because of more efficient use of air; less preheat capacity needed; easier to control and operate because of its continuous nature; more yield per unit of investment and less fumes to handle. If only one or two products are to be manufactured and if there is a continuous loading out or packaging of the product, most of these claims are quite valid. Consistant with the advantages of any continuous process, once the unit has been regulated to yield a product of constant quality, the relative high yield of a product per unit time and its cost become decided advantages. If a variety of blown asphalt grades are to be made, the continuous plant becomes less practical. Converting a continuous unit from one product to another requires considerable adjustment and sometimes manipulation of the charge stock. Most manufacturers
are called upon to make a variety of grades of blown asphalt from different fluxes, and herein lies the versatility of the batch unit and the disadvantage of the continuous unit. Batch units also require a greater investment in tankage. In spite of this, there are relatively few continuous units in operation today.

I.4.C AIR-BLOWING WITH CATALYSTS — REVIEW OF LITERATURE

The term catalytic asphalt has been accepted in spite of some question as to whether this is truly a catalytic process. Since the agents used here cannot be recovered as such, technically they might better be termed chemical reactants. In any event, the general effect is to reduce blowing time, as well as to change the softening point-penetration relationship. Reduction of blowing time is an economic incentive, whereas the change in the flow properties permits the manufacture to specifications, previously not possible.

Baillard oxidised a mixture of petroleum and oleic acid by means of air at 160°C, Busse blew air through a heated mixture of asphalt and vegetable oils in the presence of nitric acid, sulphur or sulphur dichloride. Salathe blew heated air through melted native asphalt, either alone or in the presence of litharge, Schreir proposed blowing melted asphalt
coal tar pitch, fatty acid pitch, wool fat pitch etc., with air in the presence of manganese dioxide and sulphuric acid and finally adding formaldehyde. Incidentally it is of interest to note that vaseline, liquid or solid paraffin wax may be converted into fatty acids by oxidation with potassium permanganate in an acid or alkaline solution or a mixture of manganese dioxide with hydrochloric or nitric acid.

Byerley and Mabery found that asphalts of variable properties can be obtained depending upon the temperature and the duration of the blowing process. For the softer grades (fusing under 100°C) the Lima residuum was blown three days at 200°C, during which 2% of distillate was produced. For the harder grades (fusing at about 200°C), the residuum was blown 4 to 5 days at 260°C during which between 5 & 6% of distillate was recovered. The product was claimed to be resistant to changes in atmospheric temperature, and to differ from the corresponding steam-distilled asphalt by being readily soluble in petroleum benzene or naphtha. Air under suction was passed through a 6000 gallon still of the oil, at the rate of 450 Cu.ft. per minute. Ohio petroleum residue of 21-27° Baume, also Texas Gulf coast residue of 12-15 Baume were first used for this purpose.

Hayward and Culmer obtained patents for
a similar process, according to which a mixture of petroleum residue and refined Trinidad asphalt or Gilsonite was heated to $193^\circ C$ and blown for 40 hrs at the rate of 15-30 Cu.ft. air per minute, per ton asphalt. After a time, the external source of heat was removed, since it was found that the temperature of the residue increased spontaneously, due to the chemical changes induced by the action of the air. It was also found that, the oxidation progressed very rapidly at first, and then more slowly, as it approached the end of the process. The air may either be blown through the still under pressure, or else sucked through the still by subjecting the contents of the still to a partial vacuum (upto 20 inch mercury). There are proponents of both systems. The loss depends largely upon the amount of volatile matter contained in the residual oil, and varies from practically 0 upto 10% of the weight of the charge, depending of course upon the extent the product is blown. Water and $CO_2$ are given off. It is contented that the vacuum process removes the oily and greasy matters from the residual oil and forms a brighter and cleaner looking blown asphalt. Non-asphaltic petroleums will yield a good grade of blown asphalt if first subjected to a high temperature and pressure which serve to convert saturated hydrocarbons into polymerized unsaturated compounds. It is also contented that blown asphalts
of high penetration for a high fusing point, may be produced from petrolatum, from which micro-

- crystalline wax has been separated by dissolving in a mixture of benzene and methyl ethylketone, chilling the solution, filtering, distilling off the solvent, and finally blowing the residue. Blown asphalts may likewise be produced from naphthenic residual oils or naphthenic derivatives (i.e. non-asphaltic and non-paraffinic in character) obtained by extracting petroleum with propane, S0₂, aniline, phenol etc.

Various catalysers and oxidising agents have been proposed for augmenting the air-blowing process, resulting in a product having a higher penetration for a given softening point, including finely powdered limestone, caustic soda or sodium carbonate, bentonite or finely powdered coke, sulphur, sulphuric acid with or without the addition of metallic persulphates or per borates, metallic fluoborates, boric acid, phosphoric acid or arsenious acid, P₂O₅, P₂S₅, P₄S₃, or P₄S₇, a mixture of P₂O₅ and a co-polymer of isobutylene and styrene, a mixture of H₃PO₄ and boron trifluoride, potassium chlorate, chlorides or sulphates of zinc, aluminium, iron, copper or antimony; chlorides of zinc or aluminium together with finely divided metals (e.g.: Fe, Al, Mg,
Mn or Cu, chlorides or sulphates of Zn, Al, Fe, Cu or Sb, together with a lead soap or finely divided PbO; the residue obtained in the manufacture of synthetic lubricants by polymerizing hydrocarbons (eg; olefins) with AlCl₃ as catalyst; polymerizing by heating with aluminium chloride and sulphuric acid followed by blowing with air, heating with metallic oxides, followed by blowing with air; heating with hydrochloric acid followed by blowing with air, blowing in the presence of aluminium or zinc stearate, copper, lead, cobalt, iron or chromium naphthenate, sulphonate, stearate or resinate; cobalt, chromium, manganese, iron, nickel zinc, lead or copper naphthenate or oleate in the presence of an alkali; Lead oxide (PbO) and naphthalene. First blowing with air followed by heating with a halide catalyst (eg: a halide of aluminium such as AlCl₃, a halide of boron such as BF₃, zirconium, tantalum, copper, tin, zinc, antimony, etc.) together with hydrohalogen acid (eg: HCl, HBr, HF or HI), blowing in the presence of Seleno sulphide, Thionyl perchloride, sulphuric oxyfluoride, phosphorous oxychloride, phosphorous oxy-fluoride, phosphorous thiofluoride or silicon fluoriform, a quinone dioxide, basic acetylacetonate or manganese, cerium, nickel, cobalt or zinc, copper, iron, cobalt soaps, as well as the various agents referred to previously. It has been proposed that any excess catalyst be removed after
the blowing operation by blowing the product with dilute hydrochloric acid and washing with hot water.\textsuperscript{68}

The use of various gases has been suggested for blowing through the melted asphalt including air under pressure\textsuperscript{69}, air followed by a mixture of air and steam in varying proportions under atmospheric or reduced pressure\textsuperscript{70}, carbon dioxide with or without air,\textsuperscript{71} ozone\textsuperscript{72}, a mixture of air or oxygen with NO\textsubscript{2}, or SO\textsubscript{2}\textsuperscript{73}, a mixture of air and nitrogen oxides in the presence of HNO\textsubscript{3}, carbon monoxide activated by a catalyst such as nickel or palladium, or by first heating the asphalt with cerium oxide or tin oxide and blowing as aforesaid\textsuperscript{75}, air containing up to 11.5% chlorine\textsuperscript{76}, chlorine in the presence of a "chlorine carrier" (eg: hexachlorethane\textsuperscript{77}), chlorine followed by carbon dioxide\textsuperscript{78}, bromine or boron fluoride, air and halogens in the presence of sulphur\textsuperscript{79}, air containing a trace of a gaseous catalyst (eg: SeS, SOCl\textsubscript{2}, SO\textsubscript{2}F\textsubscript{2}, POCl\textsubscript{3}, PSF\textsubscript{3}, HSiF\textsubscript{3}, POF\textsubscript{3} etc.)\textsuperscript{80}, air containing a small amount of gaseous catalyst (eg: Cl\textsubscript{2}, Cl\textsubscript{2}O, COS, NO, NO\textsubscript{2}, H\textsubscript{2}S, SO\textsubscript{2}, SO\textsubscript{3}, ethyl mercaptan, n-butyl mercaptan ozone etc.\textsuperscript{81}), air containing a trace of chlorine followed by heating with aluminium chloride etc.\textsuperscript{82}.

The blowing of different mixtures has been suggested for the purpose of improving the characteristics of the finished product, in the way of imparting
rubber like properties, greater toughness, increasing its resistance to temperature changes, augmenting its weather resistance etc. including the following, a mixture of semi asphaltic residual oil and fatty acid pitch, with or without gilsonite, a mixture of residual oil, pine tar and rubber, a mixture of residual asphalt to which latex is added, a mixture of residual asphalt with a phenolformaldehyde resin, a mixture of residual asphalt with naphthenic tar obtained upon the extraction of asphaltic or mixed base crude with phenol, furfural, cresylic acid, nitrobenzene, sulphur dioxide or the like, a mixture of native asphalt with the distillate obtained in the vacuum distillation of coal tar pitch, a mixture of residual oil or residual asphalt with vegetable drying oil, such as Soyabean oil, a mixture of residual oil and paraffin oil, a mixture of residual asphalt with cylinder oil stock, a mixture of residual asphalt and petroleum blown with air in presence of FeCl₃, a mixture of blown asphalt, cylinder oil and calcium oleate or stearate, a mixture of gilsonite, residual asphalt, and fish oil pitch, a mixture of petroleum asphalt and peat tar, mixing the blown asphalt with a co-polymer of isobutylene and styrene, treating blown asphalt with an alkyl and an alkaline earth under heat, asphalt mixed with so called "soft wax" (micro crystalline wax)
and lubricating oil\textsuperscript{101}, a mixture of asphalt with cracking still residue\textsuperscript{102}, blowing an aqueous-clay dispersion of residual oil with metallic driers at a comparatively low temperature\textsuperscript{103} blowing asphalt containing a small percent of methyl polysiloxane is claimed to increase the flash point of the blown product\textsuperscript{104} incorporating polymers of organo silicon oxide or organo Germanium oxide\textsuperscript{105}, and alternate procedure consists in heating asphalt with a substance which releases oxygen such as hydrogen peroxide, an alkyl peroxide, an arylperoxide, a tertiary butyl hydroperoxide etc.\textsuperscript{106}.

I.5 THE SCOPE OF THE PRESENT WORK

The main objectives of the investigations reported in the present thesis are the following: (1) to find out some industrial wastes as cheaper additives to augment the air-blowing polymerization process of bitumen. This will bring down the cost of production of industrial bitumen which can be applied for the manufacture of bitumenous paints, roofing and flooring materials etc. (2) to find out suitable promoters for the above additives. This will bring down the consumption of the additives (3) to help in the industrial pollution control (4) to investigate the usefulness of the industrial bitumen produced in the production of bituminous paints (5) to find out the
kinetic parameters of the reactions involved with different additives. This is essential for the design, construction and operation of new industrial bitumen plants using the additives investigated. This will also enable us to establish the mechanism of the reactions involved in the process.