COMPARATIVE STUDIES ON CATIONIC & ANIONIC EMULSIONS IN BITUMEN

A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Technology
(Refining & Petrochemical Engineering)

By

R. ARAVIND

R080207008
M.Tech. (REFINING & PETROCHEMICAL ENGINEERING)

College of Engineering
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Under the guidance of

Dr. R.P. BADONI
DISTINGUISHED PROFESSOR
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Approved

……………………………………………
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DEAN

College of Engineering
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May, 2009

UNIVERSITY OF PETROLEUM & ENERGY STUDIES

CERTIFICATE

This is to certify that the work contained in this thesis titled "**COMPARATIVE STUDIES ON CATIONIC & ANIONIC EMULSIONS IN BITUMEN**" has been carried out by **R.ARAVIND** under my/our supervision and has not been submitted elsewhere for a degree.

R.P. Badoni
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EXECUTIVE SUMMARY

Emulsions are the colloidal solution in which the both dispersion phase and the dispersion medium are liquids. Bitumen which is used for the pavements are melted and their viscosity is reduced. An alternative mechanism for reducing the viscosity of petroleum bitumen is the use of emulsion. As bitumen is immiscible with water, a stable emulsion is formed by grinding the bitumen in a mill to a particle size less than 50µm and adding it to water and emulsifier.

The two main grades of emulsion 'Cationic Rapid Setting (CRS)' and 'Anionic Slow Setting (ASS)' Emulsions are analyzed on the basis of Indian Standards. Its formation with bitumen and its parametric characteristics like viscosity, pH, Residue by Evaporation, Residue by microwave are studied and compared.

It was determined that both the emulsions are meeting the Indian Standard Specifications however, Anionic Slow Setting (ASS) emulsions are more reliable than the Cationic Rapid Setting (CRS) emulsions, and gave a future scope of study of the stability in these emulsions.

ACKNOWLEDGEMENT

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DEDICATED

To My Beloved Father 'Shri M.Ramachandran' Who Is Always with me, throughout my path

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NOMENCLATURE

ΔG_{from}	Free energy of formation of droplets from a bulk liquid
ΔA	Increase in interfacial area
γ_{12}	Interfacial tension
$T\Delta S_{conf}$	Configurational entropy contribution
U_A	Attractive force
A	Hamaker-London constant
a	Radius of spheres
H	R-2a
R	Distance between the centers of the spheres
U_R	Repulsive force
ε	Dielectric constant
a	Radius of sphere
Ψ_o	Surface potential
H	Measure of interaction between the double layers
η_r	Relative viscosity = η_d / η_c
η_c	Continuous phase viscosity (water)
η_d	Dispersed phase viscosity (bitumen)
φ	Volume fraction of the dispersed phase
φ_m	Maximum packing concentration
η	Intrinsic viscosity = 2.5 for hard sphere dispersions

INTRODUCTION:

WHAT IS CRUDE OIL?

Crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in color from clear to black. An "average" crude oil contains about,

- ✓ Carbon - 84%,
- ✓ Hydrogen - 14%,
- ✓ Sulfur - 1- 3%,
- ✓ Less than 1% of Nitrogen, Oxygen, Metals, and Salts.

Crude oil is generally classified as

- ✓ Paraffinic
- ✓ Naphthenic
- ✓ Aromatic

It is mainly based on the predominant proportion of similar hydrocarbon molecules. Mixed-base crudes have varying amounts of each type of hydrocarbon. Refinery crude base stocks usually consist of mixtures of two or more different crude oils.

Relatively simple crude oil assays are used to classify crude oils as paraffinic, naphthenic, aromatic, or mixed.

One assay method (United States Bureau of Mines) is based on distillation, and another method (UOP "K" factor) is based on gravity and boiling points. More comprehensive crude assays determine the value of the crude (i.e., its yield and quality of useful products) and processing parameters.

Crude oils are usually grouped according to yield structure.

Crude oils are also defined in terms of API (American Petroleum Institute) gravity.

The higher the API gravity, the lighter is the crude. For example, light crude oils have high API gravities and low specific gravities. Crude oils with low carbon, high hydrogen, and high API gravity are usually rich in paraffin and tend to yield greater proportions of gasoline and light petroleum products; those with high carbon, low hydrogen, and low API gravities are usually rich in aromatics.

Crude oils that contain appreciable quantities of hydrogen sulfide or other reactive sulfur compounds are called "sour crude." Those with lower sulfur are called "sweet crude."

In these types of crude, the naphthenic crude which has high wax content is used for extracting or production of bitumen.

WHAT IS BITUMEN?

Bitumen is a mixture of dark, sticky, highly viscous organic liquids composed mainly of Aromatic hydrocarbons. Bitumen found in nature is refined called crude bitumen, and the one which are obtained from distillation of crude oil is called Bitumen.

Bitumen is a non-crystalline viscous material, black or dark brown, which is substantially soluble in carbon disulphide (CS_2), possessing adhesive and water-proofing qualities.

It consists essentially of hydrocarbons and would typically comprise at least 80% carbon and 15% hydrogen, the remainder being oxygen, sulphur, nitrogen and traces of various metals.

HISTORY

Bitumen is the oldest known engineering material and has been used from the earliest times as an adhesive, sealant and waterproofing agent. As long ago as 6000BC the thriving ship-building industry in Sumeria used naturally occurring bitumen, found in surface seepage in the area.

In the Indus Valley, now in Pakistan, there is a particularly well-preserved water tank which dates back to around 3,000 BC. The stone blocks in the tank's walls are bonded with natural bitumen and there is a vertical bituminous core in the centre of the wall this same principle is used today in modern dam design. It is believed that Nebuchadnezzar was one of the early exponents of bitumen as there is evidence that he used the material for waterproofing the masonry in his palace and as grout for stone roads.

Bitumen's versatility as a construction material is unparalleled. Having been used as an adhesive, sealant and waterproofing agent for over 8,000 years,

Its uses now include:

- ✓ The construction and maintenance of roads, airfields and all areas where bitumen is used
- ✓ Roofing
- ✓ Damp proofing
- ✓ Dam, reservoir and pool linings
- ✓ Soundproofing

There appears to have been little development in materials used until the 19th century when the refining of bitumen from crude petroleum oils began. The vast majority of bitumen used by today's construction industry is refined bitumen, derived from crude oil. It is a sophisticated product available in many forms and grades developed by the bitumen industry for specific uses. The process of refining bitumen was pioneered in the early 1900s in the United States, giving rise to a myriad of contemporary industrial applications.

It is now possible to produce bitumen from non-petroleum based renewable resources such as sugar, molasses, or starch. Materials that contain bitumen are termed as bituminous coal or bituminous rock.

Bitumens are used primarily for paving roads. They have also been used for waterproofing products such as roofing felt and boats. Some have used bitumen plates to dampen the noise produced by moving computer parts and dish washers.

With the recent oil prices, it has been profitable to upgrade bitumen to synthetic crude oil. Naturally occurring bitumens have served well for the preservation of plant and animal fossils.

SOURCES

Bitumen does occur naturally, but for all intents and purposes it is petroleum on which the world relies for its supplies of bitumen today. The bitumen content of crude can vary between 15% and 80%, but the more normal range is 25% to 40%. In fact the three broad classifications for crude oils are:

- ✓ Bitumen based
- ✓ Paraffin based
- ✓ Bitumen and paraffin based

Depending on the type of crude, bitumen is present either in the form of colloidally dispersed particles or in a true solution. During the refining process, as petroleum oils are taken away by distillation, the proportion of oil to bitumen particles changes. Instead of being dispersed and relatively few in number, the particles become closer to one another and the size of the particles increases. At the point when the distillation process is usually stopped, the petroleum bitumen is a colloidal dispersion of black solids (hydrocarbons), known as **Bitumens**, in a dispersion medium, which is an oily brown yellow liquid known as **maltene** fraction. Also present to act as a stabilizing agent to keep the Bitumens in suspension are another group of hydrocarbons known as **resins**.

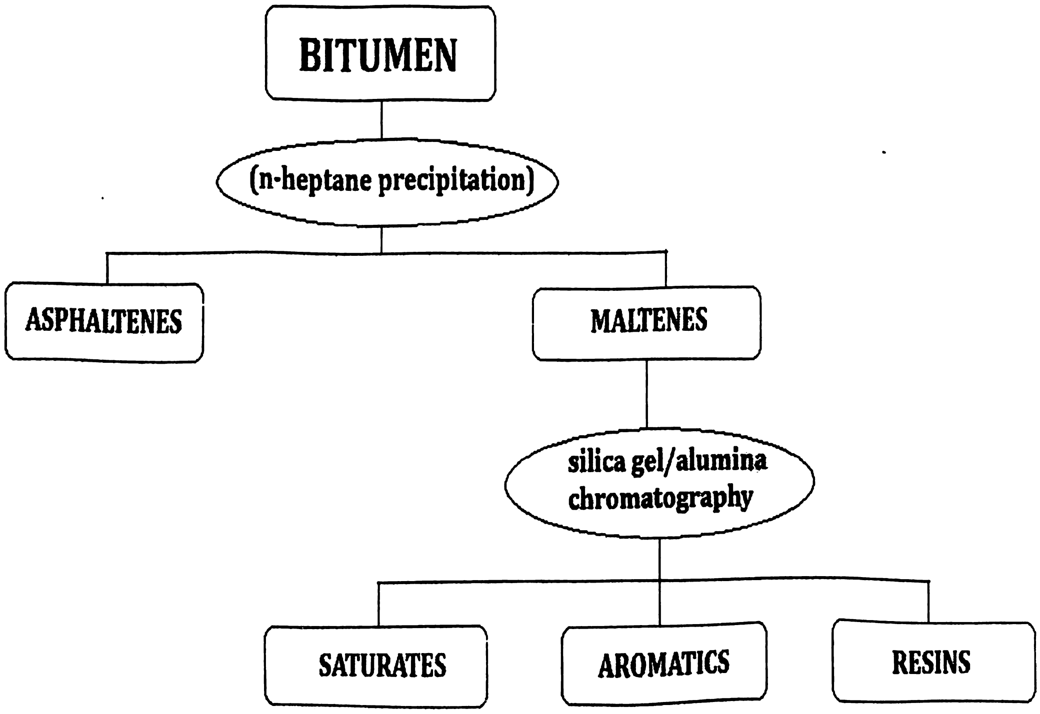


FIG 1: SEPARATION OF BITUMEN INTO VARIOUS CLASSIFICATIONS

CHEMICAL COMPOSITION

Bitumens are composed primarily of highly condensed polycyclic aromatic hydrocarbons. In addition, they contain several elements, a number of which are toxic. Examples of these elements are nickel, vanadium, lead, chromium, mercury, arsenic, and selenium. Bitumens are soluble in carbon disulfide, which is a nonpolar solvent.

Crude bitumen is a thick, sticky, tar-like form of petroleum that must be heated or diluted before it will flow. At room temperature, it is much like cold molasses. Refined bitumen is the residual (bottom) fraction obtained through the fractional distillation of crude oil.

It is the heaviest fraction and the one with the highest boiling point, boiling at 525 °C (977 °F).

Molecular weight wise, bitumen is a mixture of about 300 - 2000 chemical components, with an average of around 500 - 700. Elementally, it is around 95% carbon and hydrogen (± 87% carbon and ± 8% hydrogen), and up to 5% sulfur, 1% nitrogen, 1% oxygen and 2000ppm metals.

Given that bitumens are composed of hydrocarbons, they are flammable. For this reason, vessels for the heating of bitumen or bituminous materials are usually subject to specific conditions in public liability insurance policies, similar to those required for blow torches and welding and flame-cutting equipment.

According to the Shell Bitumen Handbook (1991) the methods available for separating bitumens into fractions can be classified as follows:

- ✓ Solvent extraction
- ✓ Adsorption by finely divided solids and removal of unabsorbed solution by filtration
- ✓ Chromatography
- ✓ Molecular distillation used in conjunction with one of the above techniques.

By means of absorption chromatography, bitumen can be separated into four functional groups with related properties with regard to chemical reactivity and rheological properties.

These generic components are generally referred to as (Shell Bitumen Handbook)

1. Bitumens
2. Resinous components (polar aromatics)
3. Non-polar aromatics (naphthene aromatics) and
4. Saturates

EMULSION – A NEW EVOLUTION IN BITUMEN

Bitumen emulsion is a stable dispersion of bitumen in water with the help of suitable emulsifying agents. In this type of dispersion, there is no need for melting the bitumen during the construction of roads, as they are viscous liquid which can easily be mixed with the aggregates at ambient temperature to construct roads.

Besides these easy and safe uses than hot bitumen, they have excellent versatility of their use on any type and nature of aggregate i.e. whether wet, cool or warm dry surface. They also have their exceptional characteristics using under high humid conditions and on cool days provided temperature do not fall below 5 ^{0}C.

The basic bitumen has also been diluted in order to facilitate application. Hot bitumen, water and emulsifier are processed in a high-speed colloid mill that disperses the bitumen in the water in the form of globules that are normally in the 5-10 µm size range but may be even smaller. The emulsifier produces a system in which fine droplets of bitumen, of between 30% and 80% of the volume, are held in suspension. If they separate in storage, the emulsion can easily be restored by agitation.

Bitumen emulsions have a low viscosity and can be workable at ambient temperatures, which makes them ideal for use in road building. This application requires controlled breaking and setting. The emulsion must not break before it is laid on the road surface but, once in place, it should break quickly so that the road can be in service again without delay.

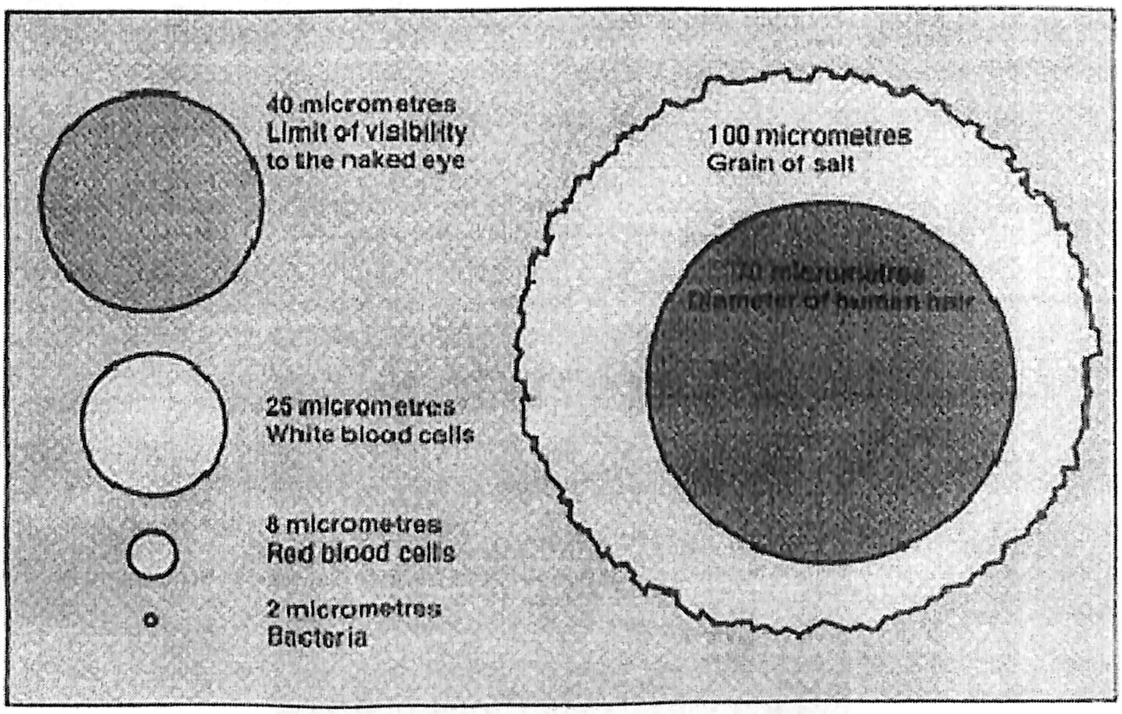


FIG 2: PARTICLES OF BITUMEN DISPERSED IN WATER TO MAKE BITUMEN EMULSIONS ARE USUALLY BETWEEN 5 AND 10µmIN SIZE. THE DIAGRAM DEPICTED ABOVE REPRESENTS THE RELATIVE SIZE

EMULSION CHEMISTRY

An emulsion can be defined as a dispersion of small droplets of one liquid in another liquid. Bitumen emulsions belong to the oil-in-water type of emulsion where bitumen is dispersed in water.

The size of the droplets is generally in the range of 0.001 to 0.01mm. The bitumen content depends on the intended application of the emulsion, but is rarely lower than 30% or higher than 70%.

There is an upper limit to the bitumen content of an emulsion, which mainly depends on the relative volume of the two phases.

When reaching the limit there is insufficient room for the droplets. The droplets will be packed so tightly that they will partly adhere to each other and eventually the water entrapped between the droplets.

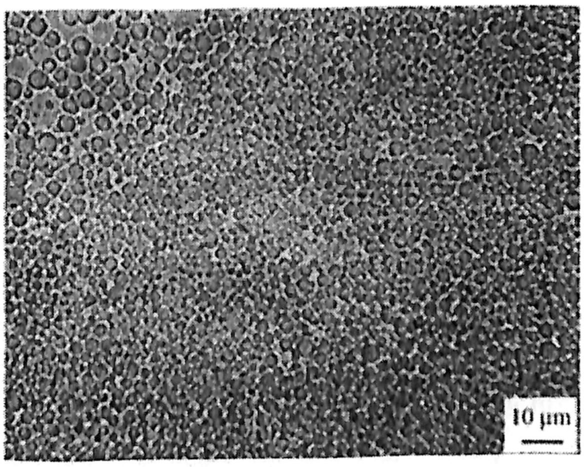


FIG 3: BITUMEN IN WATER (OIL-IN-WATER) EMULSION

The result will be water–in-oil emulsion, or inverted emulsion, such as emulsion has the nature of bitumen, with high viscosity.

The limit of bitumen content is in the range of 70% to 80% and depends mainly on the size distribution of the particles.

CLASSIFICATION OF EMULSIONS

As emulsions are colloidal dispersions where both the dispersion phase and the dispersion medium are in oil or liquid phase, they are mainly classified into two major types as follows:

- ✓ Water-in-oil Emulsions
- ✓ Oil-in-water Emulsions

In water-in-oil emulsions, the dispersion medium is Oil and the dispersion phase is the water.

And in Oil-in-water emulsions, the dispersion medium is water and the dispersion phase is oil.

It has been proved that it easy to separate or demulsify the first type of emulsion that is water-in-oil emulsion, but not possible to carry out the same for the oil-in-water emulsions.

Thus the oil-in-water emulsions are studied and are now of different commercial applications all over the world.

One of the main examples of this oil-in-water emulsion is Bitumen Emulsions.

Bitumen emulsion which is of oil-in-water emulsion is sub-categorized as follows:

- ✓ Anionic emulsions with negatively charged globules
- ✓ Cationic emulsions with positive charged globules
- ✓ Non-ionic emulsion with neutral globules

The anionic and cationic emulsions are mainly in application of road or pavement construction and maintenance.

The third category that is the non-ionic emulsion is not in that much use. Many researches are going on it, which will come to its commercial use in a very advance periods of emulsion technology.

When the two poles (anode and cathode) are immersed in a liquid, and electricity is passed through it, the anode gets charged positively and the cathode gets charged negatively.

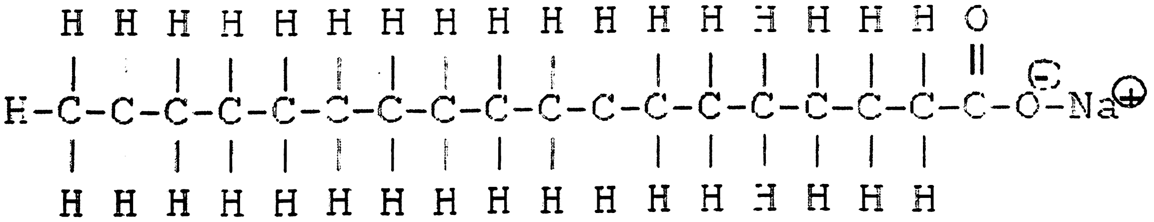
ANIONIC EMULSIONS

If the current is passed through the emulsion which has negatively charged particles of the bitumen, they will migrate towards the anode. Thus the emulsion as referred to as **Anionic Emulsion.**

In an anionic emulsion, there are numerous amounts of bitumen droplets with emulsifying agent in water-bitumen interface.

The tail portion of the emulsifying agent aligns itself in the bitumen while the positive portion of the head floats around in the water leaving the rest of the head negatively charged and at the surface of the droplet. This imparts a negative charge to all the droplets. Since negatives repel each other, all the droplets repel each other and remain as distinct bitumen drops in suspension.

A typical anionic emulsifying agent is shown below along with a diagram showing the orientation of the agent at the bitumen-water interface and the negative charge imparted to each drop.



Where the electrovalent and polar hydrocarbon group is part of the negatively charged ion, when the compound ionizes:

ANIONIC

$CH_3\,(CH_2)_n\,COO^-Na^+$

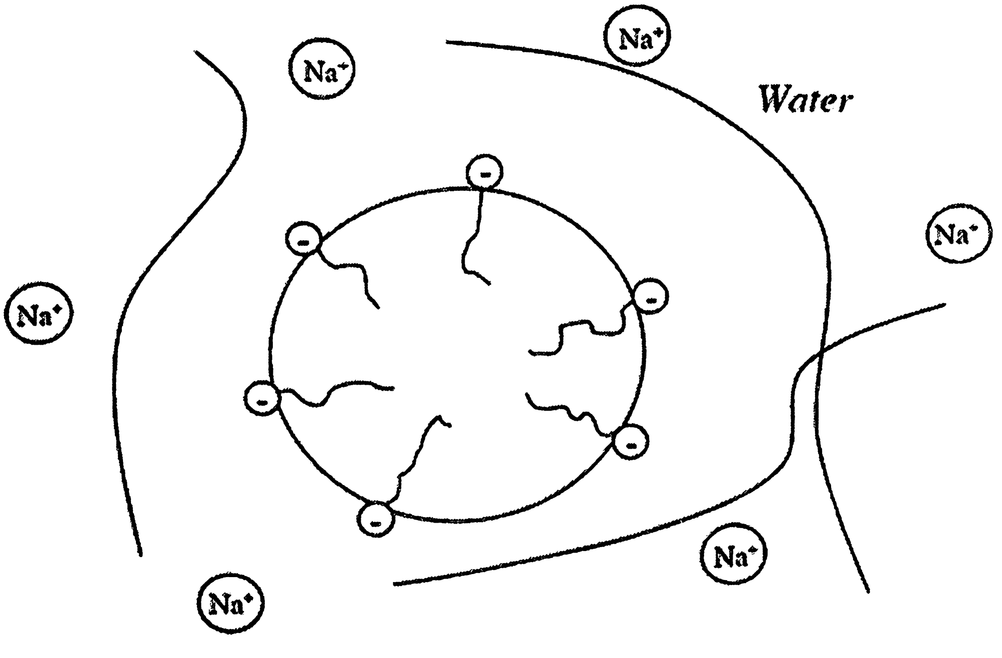
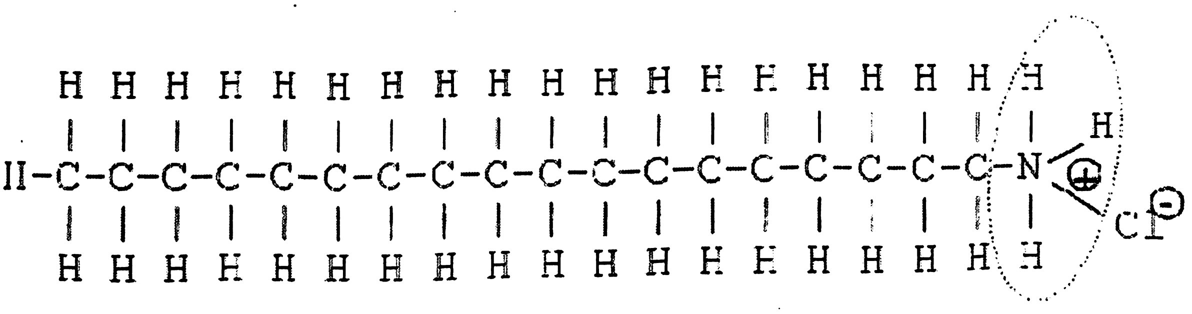


FIG 4: STRUCTURE OF ANIONIC EMULSION AND ACTION OF ITS EMULSIFYING AGENT

CATIONIC EMULSIONS

If the current is passed through the emulsion which has positively charged particles of the bitumen, they will migrate towards the cathode, which is positively charged. Thus the emulsion is called Cationic Emulsion.

The cationic emulsifying agent functions similarly to the anionic; the negative portion of the head floats around in the water leaving a positively charged head. This imparts a positive charge to all the droplets. Since positives repel each other, all the droplets repel each other and remain as distinct bitumen drops in suspension. A typical cationic emulsifying agent is shown below along with a diagram showing the orientation of the agent at the bitumen-water interface and the positive charge imparted to each drop.



Where the electrovalent and polar hydrocarbon group is part of the positively charged ion when the compound ionizes:

CATIONIC

$CH_3 (CH_2) NH_3$ +Cl

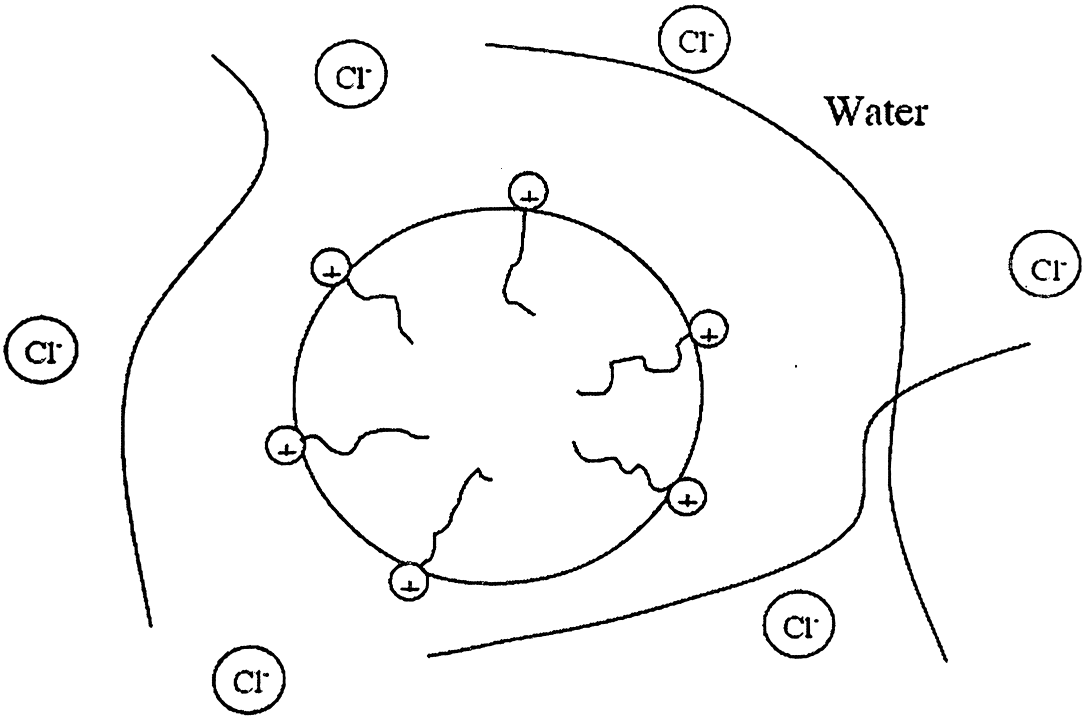


FIG 5: STRUCTURE OF CATIONIC EMULSION AND ACTION OF EMULSIFYING AGENT

The Bitumen emulsions, cationic and anionic are further classified into three types based on the grades of which the emulsions are produced.

They are as follows:

- ✓ Rapid Setting (RS)
- ✓ Medium Setting (MS)
- ✓ Slow Setting (SS)

The classifications of bitumen emulsions on their grades are:

ANIONIC EMULSION	CATIONIC EMULSION	GRADES
ARS	CRS	Rapid Setting (RS)
AMS	CMS	Medium Setting (MS)
ASS	CSS	Slow Setting (SS)

TABLE 1: GRADES OF BITUMEN EMULSION (ANIONIC & CATIONIC)

APPLICATION OF THE EMULSIONS

Recommeded Grade	ARS/ 60	AMS/ 60	ASS/ 60	CRS/ 60	CRS/ 67	CMS/ 60	CSS/ 60
Application							
Sprayed seal	●			●	●		
Tack Coat	●	●	●	●		●	
Primer seal				●	●		
Prime							
Surface enrichment			●	●		●	●
Recycling		●	●			●	●
Maintenance work	●			●			
Cold Mix			●			●	●
Slurry surfacing			●				●
Pavement stabilisation		●	●			●	●
Soil stabilisation			●				●
Batter stabilisation			●				●
Dust laying			●				●

TABLE 2: APPLICATIONS OF VARIOUS GRADES OF EMULSIONS

PRODUCTION OF EMULSIONS

The basic equipment to prepare an emulsion includes a high-speed, high-shear mechanical device (usually a colloid mill) to divide the bitumen into tiny droplets. Also needed are an emulsifier solution tank, heated bitumen tank, pumps, and flow-metering gauges.

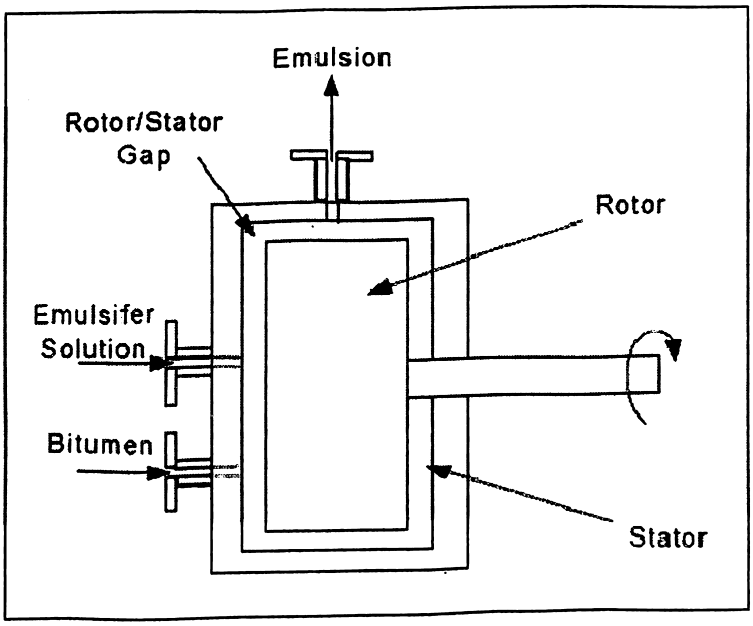


FIG 6: PRODUCTION OF BITUMEN EMULSION

The colloid mill has a high-speed rotor that revolves at 17 - 100 Hz (1,000 - 6,000 rpm) with mill clearance settings in the range of about 0.25 - 0.50 mm (0-01 - 0.02 in.). Typically bitumen emulsions have droplet sizes smaller than the diameter of a human hair, or about 0.001 - 0.010 mm (0.00004 - 0.0004 in.). Particle size analyzers are commonly used to characterize emulsion quality. Bitumen droplet sizes depend upon the mechanical energy density imparted by the mill.

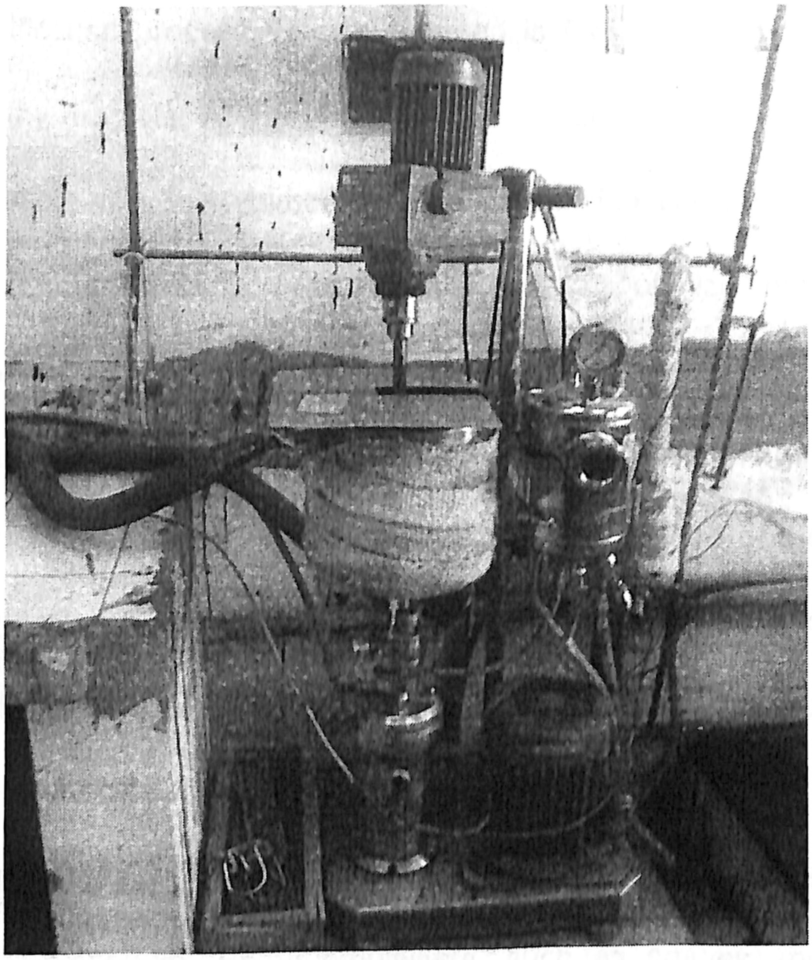


FIG 7: A PICTORIAL VIEW OF HIGH-SPEED SHEARMETER. (COURTESY: IIP, DEHRADUN)

Separate pumps are used to meter bitumen and the emulsifier solution into the colloid mill. Because the emulsifier solution can be highly corrosive, it may be necessary to use equipment made of corrosion resistant materials.

EMULSIFYING PROCESS:

In the emulsification process, heated bitumen is fed into the colloid mill where it is divided into tiny droplets. At the same time, water containing the emulsifying agent is fed into the colloid mill. The bitumen entering the colloid mill is heated to a low viscosity, and the water temperature is also adjusted to optimize emulsification. These temperatures vary and depend upon the emulsification traits of the bitumen cement and the compatibility between the bitumen and the emulsifying agent. Extremely high bitumen temperatures are not used because the temperature of the emulsion leaving the mill must be below the boiling point of water, unless a heat exchanger is used to cool the emulsion. The emulsion is then usually pumped into bulk storage tanks. These tanks may be equipped with mechanical agitation to keep the emulsion uniformly blended. The method of adding the emulsifier to the water varies according to the manufacturer's procedure. Some emulsifiers, such as amines, must be mixed and reacted with an acid to be water soluble. Others, such as acids, must be mixed and reacted with an alkali to be water soluble. Emulsifier mixing is typically done in a batch mixing tank.

The emulsifier is introduced into warm water containing acid or alkali and agitated until completely dissolved.

Bitumen and emulsifier solution must be proportioned accurately. This is normally done with flow meters, but monitoring the temperature of each phase and the mill discharge can also control the proportioning. If temperature regulation is used, the desired outlet temperature of the finished emulsion is calculated from the various emulsion ingredients and then used to control the bitumen content percentage.

CHARACTERISTICS OF BITUMEN EMULSIONS

The bitumen emulsions that are produced are of different grades and have factors to get categorized and characterized.

The main characteristics of these obtained bitumen emulsions are as follows:

- ✓ Viscosity
- ✓ Settlement
- ✓ Flocculation
- ✓ Coalescence
- ✓ Breaking
- ✓ Adhesion

VISCOSITY

Viscosity is defined as the resistance to flow of a fluid. The viscosity must be predictable and remain within certain limits throughout the storage life of the emulsion. Many factors have an influence of the viscosity, as follows:

- ✓ Bitumen content
- ✓ Temperature of emulsion
- ✓ Droplet size distribution

SETTLEMENT

Settlement is a process, where the bitumen phase or part of it moves towards the bottom of the emulsion container. The fact that an emulsion settles does not necessarily mean that it is unstable-gentle agitation often the emulsion back to original quality.

Settlement in an emulsion is due to the gravity force and the difference in density between the two phases.

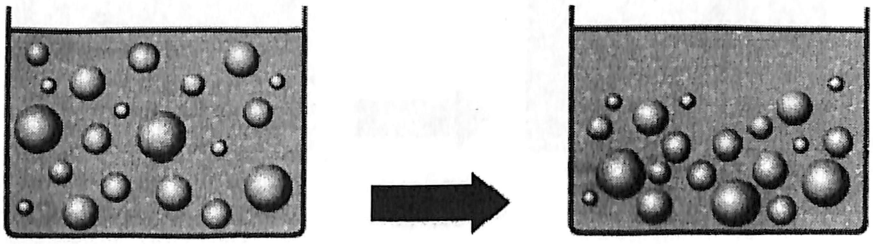


FIG8: SETTLEMENT

FLOCCULATION

Flocculation is a process where the droplets start adhering to each other. Very often there is a large central droplet with smaller droplets surrounding it. Flocculated droplets can often be separated again by agitation.

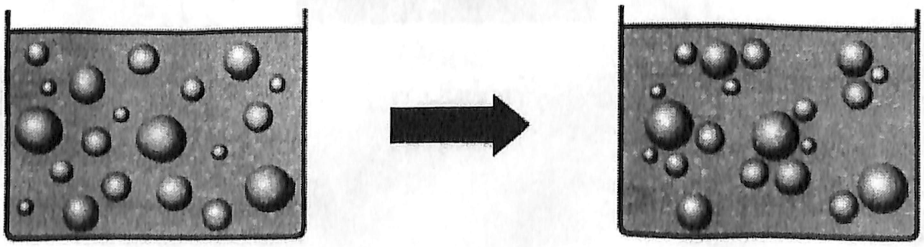


FIG9: FLOCCULATION

COALESCENCE

When droplets in an emulsion merge to form bigger droplets, it is thus called coalescence. Flocculation is often followed by coalescence. Coalescence can be started because of mechanical action such as agitation, pumping and vibration. Coalescence occurs in the breaking process and is dependent on the aggregate type.

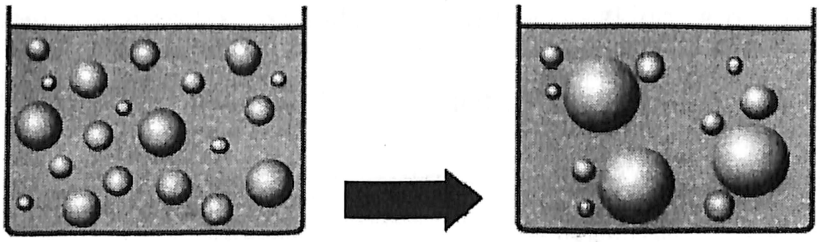


FIG10: COALESCENCE

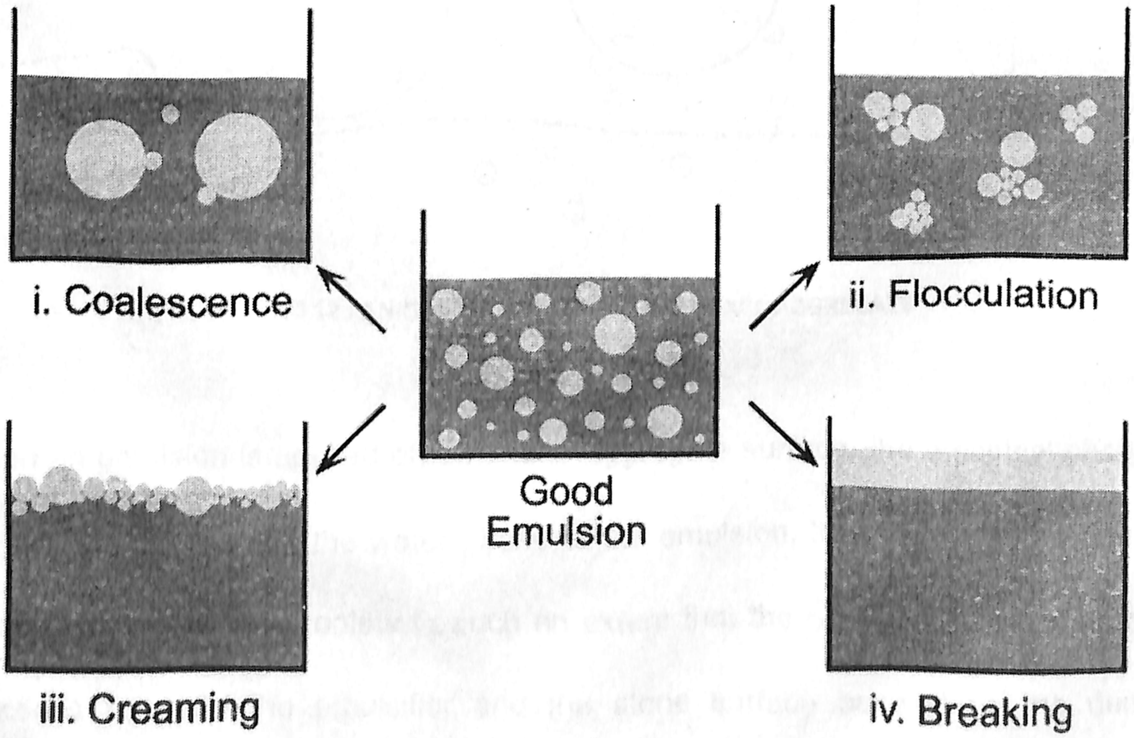


FIG11: CHARACTERISTICS OF BITUMEN EMULSION

BREAKING

The main purpose of emulsifying bitumen is to transfer it to a fluid state at ambient temperature. The emulsion should be stable during storage and transport but when applied in mineral aggregate or pavement surfaces, it should break, at a predetermined rate. The rate of breaking is largely controlled by the type and dosage of emulsifier. Other factors, however also has an influence on the breaking rate, Such as the type of aggregate, the temperature and the other climatic conditions.

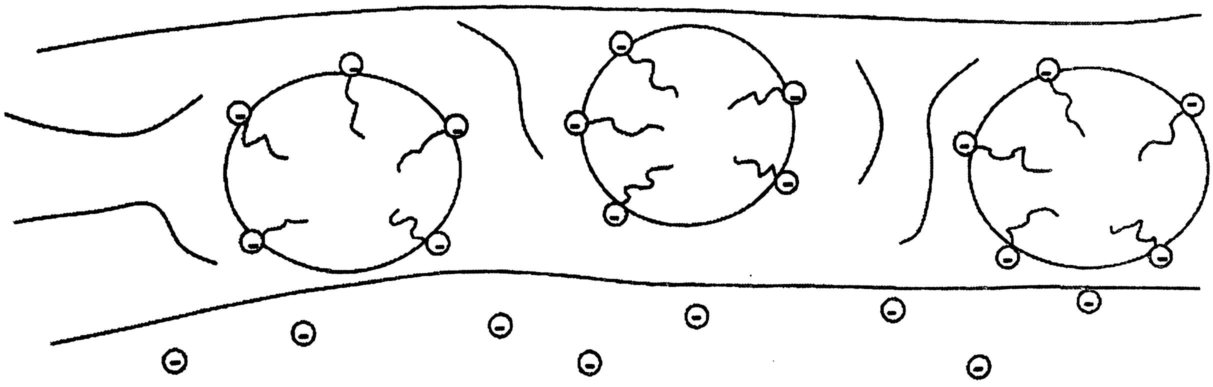


FIG 12 : ANIONIC EMULSION WITH SURFACE AGGREGATE

When an emulsion is applied on a mineral aggregate surface, the electrical charges on the emulsifier ions from the water phase of the emulsion, thus reducing the number of emulsifier ions on the droplets to such an extent that the breaking process starts. The reactions between the emulsifier and the stone surface as well as the described equilibrium are influenced by temperature.

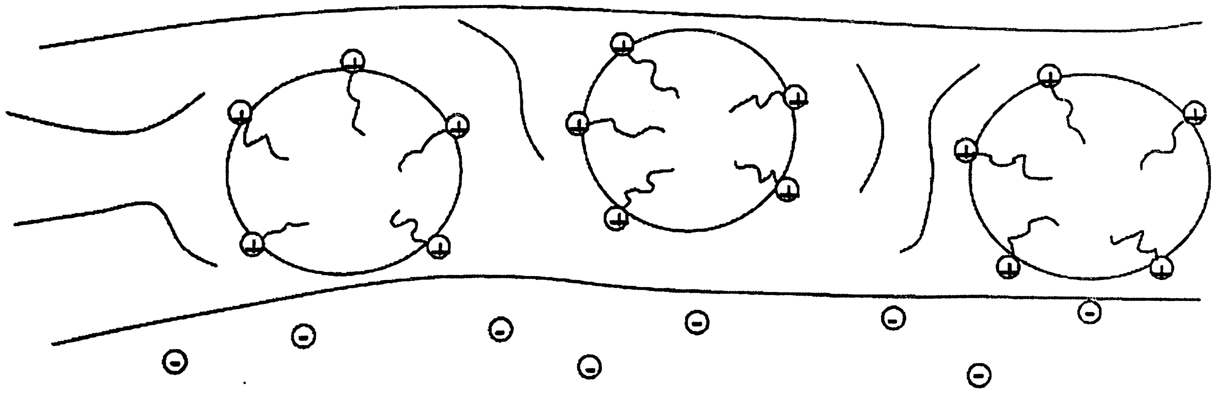


FIG 13 : CATIONIC EMULSION AND THEIR SURFACE AGGREGATES

Since most aggregate used in road construction have a majority of negative charges on its surface, cationic emulsion are generally more suitable than anionic.

Climatic conditions apart from the ambient temperature, such as relative humidity and wind velocity affect the evaporation of the water phase. Breaking can also be accelerated by mechanical forces, for example by vibration from a roller or even traffic.

ADHESION

Adhesion is the logic result of breaking.

For anionic emulsion with acidic aggregate, e.g. silica, it is the inorganic cation (K^+ of Na^+) in the emulsifier which absorbed on the surface of the silica. This cation does not give an oleophilic property to the surface on which it is absorbed and moreover has no surface active effect. The resultant adhesion is therefore poor.

On the other hand, a cationic emulsion breaking on acidic or basic aggregate results in a strong absorption of the organic cation $R\text{-}NH_3^+$ on the surface. This cation gives oleophilic property to the surface on which it is absorbed, and has water displacing effect resulting in strong adhesive of the deposited bitumen film to the aggregate surfaces. In this way cationic emulsions act as anti-stripping agents after breaking of the emulsion.

THERMODYNAMICS OF EMULSIONS OF BITUMEN

The produced emulsion is thus formed by two basic steps, i.e.

- ✓ Formation of droplets
- ✓ Droplet stabilization

The formation of the bitumen emulsion is completely unfavoured process thermodynamically.

In the first step, unstable dispersed phase is produced by disturbing the stable bulk liquid. In the second step, the stable bulk liquid is reformed by the droplets as it coalesces immediately.

FORMATION OF EMULSIONS

The vibrant usage of emulsifying agents creates a metastable condition of the produced emulsions which are thermodynamically unstable.

The emulsifiers initially lower the interfacial tension for easy formation of fine dispersion droplets.

The formation of new droplets is given by the surface forces,

$$\Delta G_{form} = \Delta A\gamma_{12} - T\Delta S_{conf}$$

The decrease in the interfacial tension reduces the energy required to for new droplets or emulsions thus making the process thermodynamically stable.

EMULSION STABILIZATION

The emulsifiers also help the droplets for its stability by forming a protective coating around the droplets and prevent coalescence. These agents have a polar head and long non-polar chain. The chains of the agents orientate themselves such that the polar head surrounds the non-polar molecule and are known as micelles.

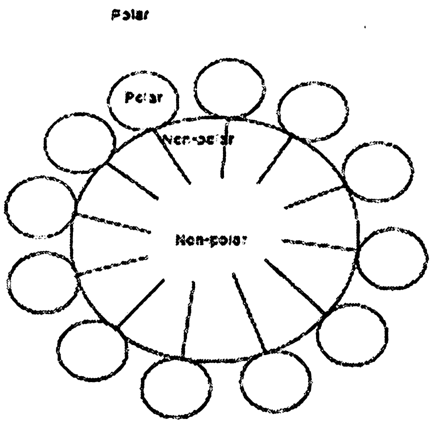


FIG 14: THE STABILISED OIL DROPLET IN WATER

THEORY OF STABILIZATION

Both short and long range forces are important in the determination of the stability of an emulsion. Short range forces determine the structure of the interface while long range forces may be used to determine if an emulsion will demulsify. Short range forces include:

✓ Chemical bonding of molecules to surface groups

✓ Physical attachment by dipole interaction

✓ Hydrophobic bonding

✓ Repulsion forces

Important long range forces include:

✓ London-van der Waals attractive forces

✓ Repulsive electrical double-layer forces

London-van der Waals attractive forces may be approximated to:

$$U_A = -Aa / 12H$$

Where:

UA - Attractive force

A - Haymake-London constant

a - Radius of spheres

H - R-2a

R - Distance between the centers of the spheres

Repulsive electrical double-layer forces are defined as:

$$U_R = 0.5\varepsilon a\Psi_o \ln[1-\exp(-kH)]$$

Where:

U_R - Repulsive force

e - Dielectric constant

a - Radius of sphere

Ψ_o - Surface potential

K - Debye Parameter

H - Measure of interaction between the double layers

GIBBS - MARANGONI EFFECT

If the surfactant is in the continuous phase, coalescence of newly formed droplets may be prevented by the Gibbs-Marangoni effect. If the droplets move towards each other but are insufficiently covered by surfactant, they will acquire more surfactant at their surface during their approach. The amount of surfactant available for adsorption will be the lowest between the droplets where the film between the droplets is the thinnest. This variation in the distribution of the surfactant leads to an interfacial tension gradient. The interfacial tension is highest where the surface excess is the lowest.

The interfacial gradient causes streaming of the surfactant along the surface of the droplets and drives the particles away from each other. This movement of surfactant works as a self stabilizing mechanism for the emulsion and is responsible for preventing coalescence.

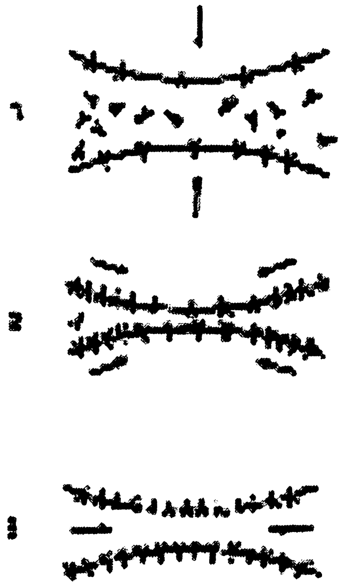


FIG 15: GIBBS MARANGONI EFFECT ON TWO APPROACHING DROPLETS

Step I - Surface has insufficient surfactant coverage

Step 2 - Surface acquires more surfactant as the drops approach each other

Step 3 - Surfactant moves along gradient and drives droplets away from each other

PROPERTY CHARACTERIZATION OF EMULSIONS

Several different properties are used to characterize emulsions. These characteristics may then be utilized in determining the stability of an emulsion. Some useful properties for characterizing emulsions include:

- ✓ Rheology
- ✓ Size distribution of dispersed phase
- ✓ Demulsification mechanisms
- ✓ Concentration of phases
- ✓ Zeta Potential
- ✓ Stability
- ✓ Conductivity

Emulsion stability is favoured by the following characteristics:

- ✓ Small droplet size
- ✓ High viscosity
- ✓ Low interfacial tension
- ✓ Electric double layer repulsion

RHEOLOGY

The Rheology is an important property to characterize the bitumen emulsion as it is mainly studied by the viscosity of various emulsions.

The rheological properties of the bitumen emulsions depend on:

Bitumen volume fraction

- ✓ Particle size
- ✓ Size distribution
- ✓ Nature of the emulsifying agent

BITUMEN VOLUME FRACTION

The volume fraction of the dispersed phase has been identified as the most important factor that influences the viscosity of an emulsion (Lee, et al., 1997). This study considered water-in-oil emulsions and determined that at dispersed phase concentrations above the maximum random packing concentration of $\varphi = 0.64$, a network structure is formed which leads to a dramatic increase in the viscosity of the emulsion. This study also determined that at dispersed phase concentrations of about $\varphi = 0.49$ the morphological structure has little effect on the rheological properties of the emulsion. Although random packing best describes the morphological state of bitumen emulsions, it is useful to realize the volume fraction of close-packed mono dispersed spheres is $\varphi = 0.7405$, the volume fraction of body centered cubic packing is $\varphi = 0.68$ and the volume fraction of face centered cubic packing is $\varphi = 0.74$.

Some studies have tried to quantify the effect of bitumen volume fraction on the rheological properties of an emulsion. These studies suggest emulsion viscosity increases sharply with the increase in volume concentration of the dispersed phase Correlations were developed from these studies to estimate the emulsion viscosity from the volume fraction of the emulsion. Some of these correlations are presented below.

The Krieger-Dougherty equation:

$$\eta_R = [\,1-\varphi/\varphi_m]^{\eta\varphi_m}$$

Where:

η_r - Relative viscosity = η_d/η_c

η_c - Continuous phase viscosity (water)

η_d - Dispersed phase viscosity (bitumen)

φ - Volume fraction of the dispersed phase

φ_m - Maximum packing concentration

η - Intrinsic viscosity = 2.5 for hard sphere dispersions

Unfortunately it is difficult to determine fm for emulsions and this model is limited to Newtonian systems.

Chong et.al (1971) estimated φ_m by plotting φnr/ (nr-1) versus φ and extrapolating the straight line to a point where the two variables become equal (Pal, 1997) and developed:

$$\eta/\eta_0 = [1+0.75\,((\varphi/\varphi_\infty)/\,(1-\varphi/\varphi_\infty)]$$

Where:

$\eta/\eta 0$ - relative viscosity

ϕ - 0.605

Other correlations were developed which relate the relative viscosity of the emulsion to the particle Reynolds number, the volume fraction of the dispersed phase, the intrinsic viscosity and the maximum concentration of the dispersed phase. For low concentrations ($\varphi_m < 0.7$) this correlation is defined as:

$$\phi_m^{1/2}[1-\eta_r^{-1/[\eta]}] = A_0 + A_1 \log_{10}(N_{Re,p})$$

Where $N_{Re,p} = \rho_c \gamma R^2/\eta_c$

ηc - Continuous phase viscosity (water)

ηd - Dispersed phase viscosity (bitumen)

K - Relative viscosity = $\eta d/\eta c$

η - Intrinsic viscosity = 2.5 [(K+0.4)/ (K+1)]

ρc - Continuous phase density

R - Particle radius

ϕm - Maximum packing concentration

γ - Shear rate

A0, A1 - Empirically determined constants

For oil-in-water emulsion A0 and A1 can be interpolated as 5.12x10-1 and –2.79x10-2 respectively. This correlation can be rearranged and used to predict the average particle size of an emulsion). φ_m may be determined from the size distribution data as 0.92 using:

$$\phi_m = \frac{\sum D_i^3 f_i}{\sum (D_i \sim D)^3 + \frac{1}{\beta} \sum [(D_i + D)^3 - (D_i \sim D)^3] f_i}$$

$$\beta = 1 + \frac{4}{13}(8\phi_{mo} - 1) D \frac{\sum (D_i + D)^2 \left[1 - \frac{(3/8)D}{(D_i - D)}\right] f_i}{\sum [D_i^3 - (D_i \sim D)^3] . f_i}$$

Where:

ϕ_m^0 - maximum packing concentration of mono disperse emulsion = 0.74

D - Number average diameter

fi - number fraction of droplets of diameter Di

(Di ~ D) = 0 for Di < D

= Di - D for Di > D

As this calculated value of φ_m seems much too high, a value of φ_m = 0.64 was used instead.

SIZE DISTRIBUTION

The viscosity of an emulsion increases as the width of the size distribution decreases. If the emulsion has a wide size distribution the small droplets are able to fit in the voids between the large droplets and disturb the network structure of the large particles. The particles become more mobile once the network is disturbed making the emulsion less stable and decreasing the viscosity. Emulsions with different size distributions could be the result of different mixing environments when the emulsions are initially formed. If there is a low interfacial tension between the aqueous and the bitumen phases, the dispersed bitumen is more likely to form small droplets as this is more thermodynamically stable.

NEWTONIAN BEHAVIOUR

Rheology can also be used to determine the bulk viscosity properties. Oil in water emulsions are generally Newtonian at low bitumen concentrations and may have a yield stress. At higher concentration, oil in water emulsions is often pseudo plastic. Bitumen emulsions show pseudo plastic behavior. This behaviour does not influence the stability of the emulsion but helps to characterize the emulsion.

LOSS AND STORAGE MODULI

In simple fluids, the frequency dependence of the storage (G') and loss (G") moduli is generally described as G' ~ w2 and G" ~ w or that a plot of log G' or log G" against log w will have a gradient of 2 and 1 respectively. Deviations from this behavior indicate the presence of a weak internal structure. In previous studies, the relationship between frequency and storage and loss moduli was determined as G' ~ w1.5 and G" ~ w0.7.

The storage and loss moduli have also been used to determine changes in the morphological state of emulsions (Lee, et al., 1997). A plot of log (storage modulus) versus log (loss modulus) shifts to the left as the particles are broken up. Presumably a shift to the right indicates that the particles are flocculating. The following figure shows the shift in the curve as the morphological state changes. The circles and squares show the state of the emulsion before preshear and at low preshear rates while the triangles depict the effect of particle break up on the morphology of the emulsion.

NUCLEAR MAGNETIC RESONANCE

The stability of an emulsion may be indirectly determined through Nuclear Magnetic Resonance (NMR). NMR measures the extent of oil solidification during the cooling of an emulsion. The amount of oil that solidifies is directly related to the stability of the emulsion. Emulsions which show little super cooling are generally unstable whereas those that are resistant to oil solidification are also stable to creaming and phase separation.

NMR is also used to monitor emulsion droplet formation and destabilization and can differentiate between large single droplets and clusters of smaller droplets. This technique uses the fact that the diffusion of oil molecules within the oil-in-water emulsion droplets results in the attenuation of a coherent magnetic signal that emanates from those droplets. This technique is well suited to monitor coalescence and flocculation processes.

DIFFERENTIAL SCANNING CALORIMETRY

The Differential Scanning Calorimetry (DSC) technique determines the quantity and the freezing characteristics of the dispersed water phase. These properties provide an indication of the extent of droplet coalescence and therefore the stability of the emulsion. The dispersed phase is determined as the difference between the total amount of water and the non-freezable water. Non-freezable water (bound water) has properties differing from the bulk due to interaction between the water and the dispersed phase and will not freeze when the sample is cooled to at least – 70°C.

ASPHALTENES AND RESINS CONTENT

The stability of emulsions has also been attributed to the resins content to asphaltene content ratio (r/a). Bitumens with a high r/a ratio (i.e. greater than 3) tend to give stable emulsions while bitumens with a low r/a ratio (i.e. less than 2) generally produce unstable emulsions.

EXPERIMENTAL ANALYSIS

The two samples of Cationic Rapid Setting Emulsion and Anionic Slow Setting Emulsion are taken and are used for the tests of:

- ✓ Viscosity
- ✓ pH
- ✓ Residue by Evaporation
- ✓ Residue by Microwave

These tests are performed for both the samples of emulsions and their comparisons are studied and the emulsion which is most suited for various applications are suggested based on its characteristics.

The samples of the two emulsions are prepared at A.R.THERMOSETS PVT.LTD, KANPUR. And the experiments are conducted for one week in the company. The variations for each day are examined and its results comprising of discussions are as follows.

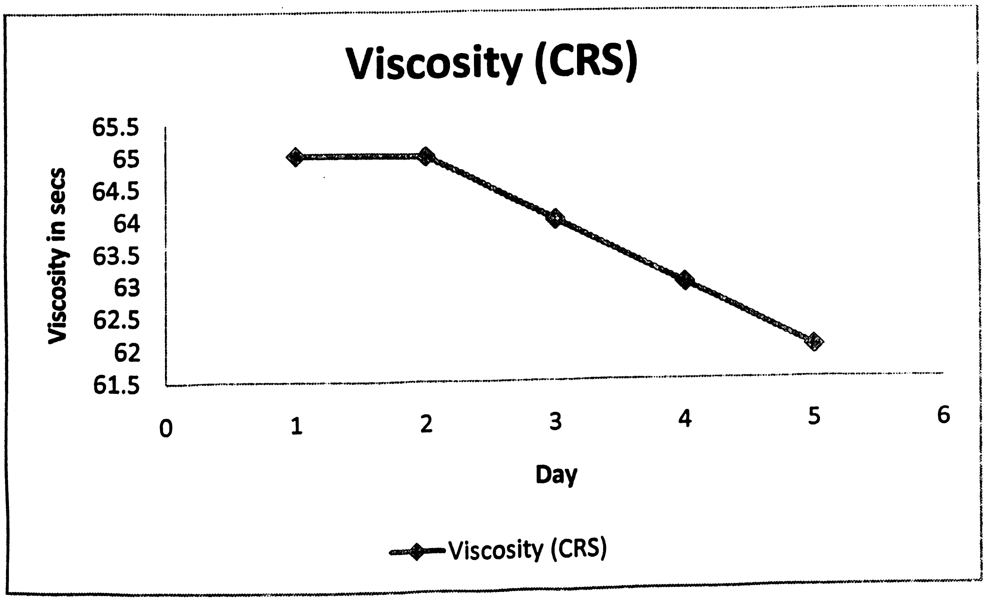
TEST WITH VISCOSITY

The Cationic emulsion sample is taken in a 100ml beaker and the experiment is conducted by using Saybolt viscometer

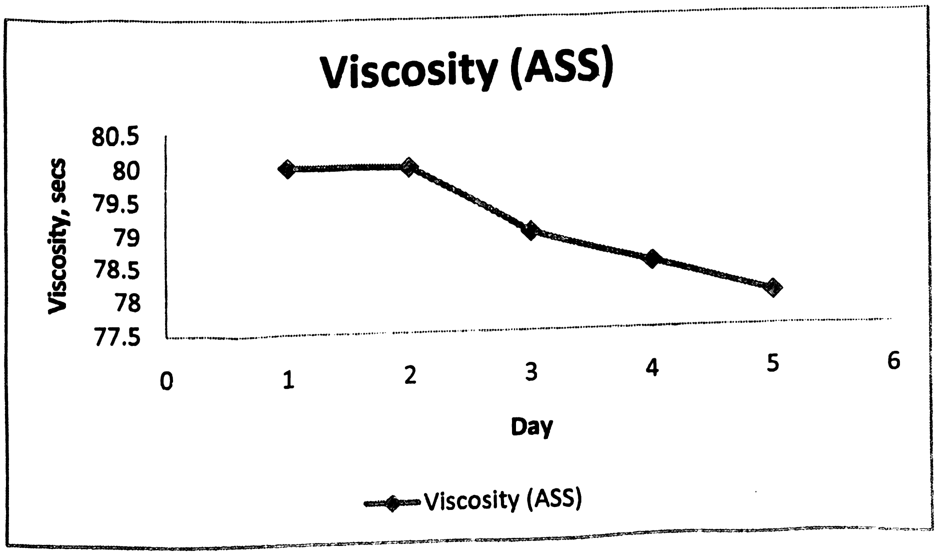
The sample is taken in the viscometer, and is locked at one side with the finger or a small tube to fill in the sample. The lock is now released to see the flow of emulsion through the Saybolt viscometer and the time for crossing the two marked ends is noted.

These readings are taken for five days both morning and evening for better results. The same procedure is followed for the anionic emulsions also.

The results which are obtained are plotted into the graph which is shown below.



GRAPH 1: VISCOSITY VARIATIONS FOR CRS



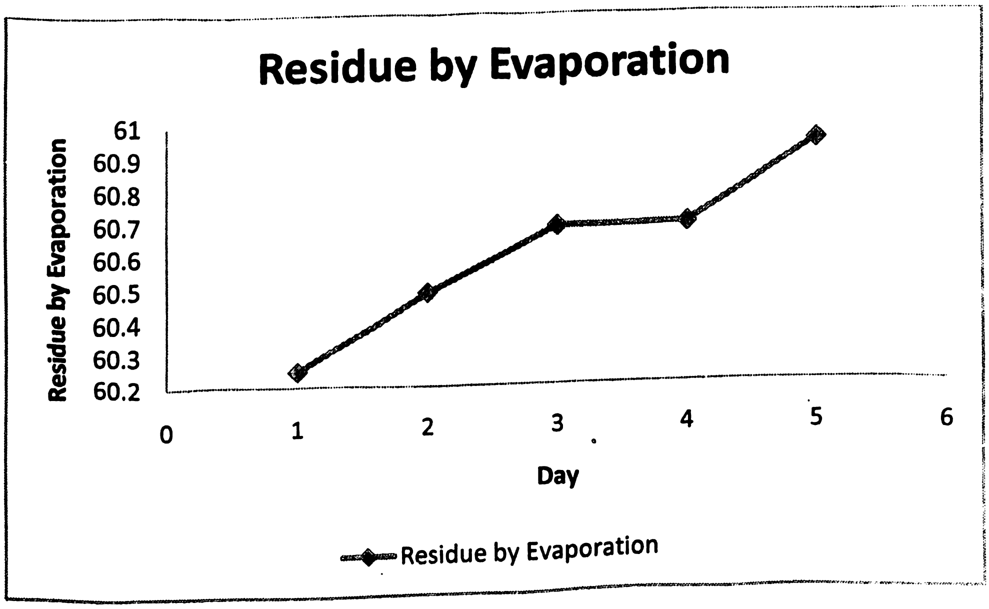
GRAPH 2: VISCOSITY VARIATIONS FOR ASS

The seeing the above plots, it is observed that viscosity of the cationic emulsion is normally lower than that of Anionic emulsions and the viscosity rapidly set down when compared to the anionic emulsions.

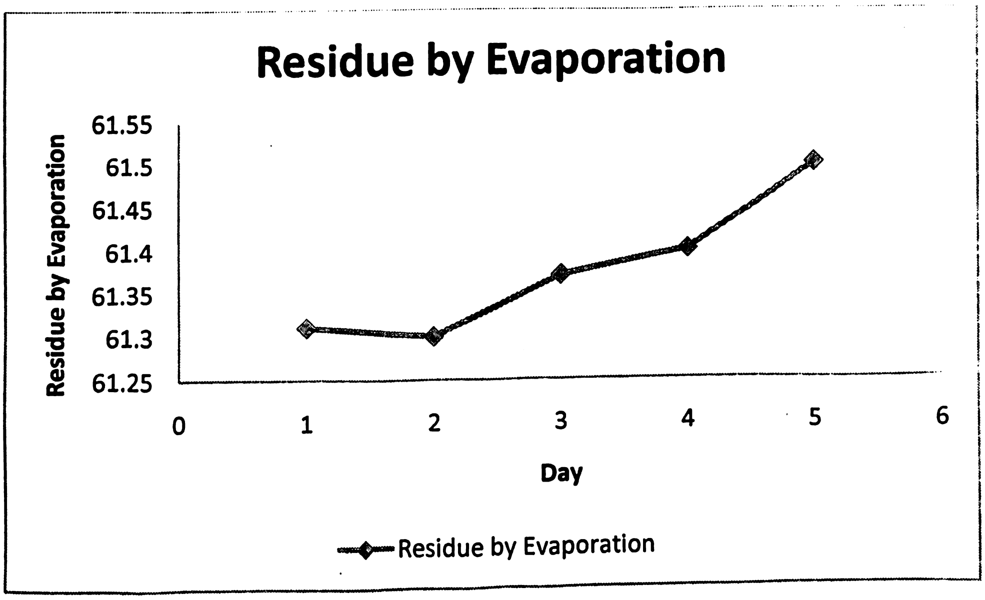
RESIDUE BY EVAPORATION & MICROWAVE

A 100g of the sample is weighed and is kept in a heater for about some minutes until the temperature reaches 100°C. Then the amount which is limited in the beaker after all the loss of moisture and water content in the emulsion. These readings are compared for both Cationic and Anionic emulsions.

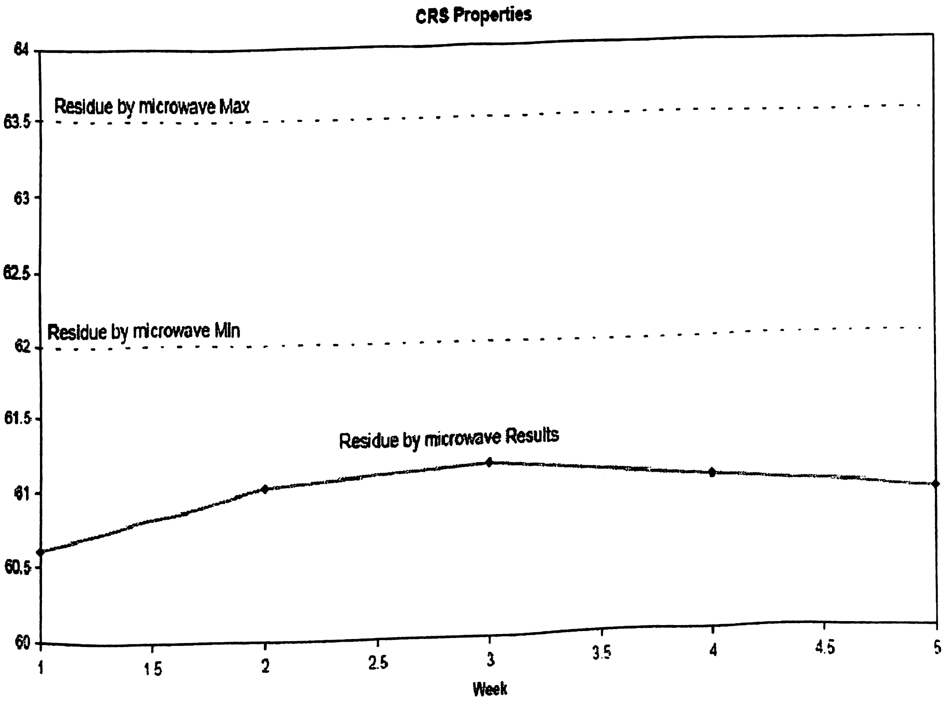
The same procedure is done by heating the emulsion in a microwave oven and the results are declared as follows.



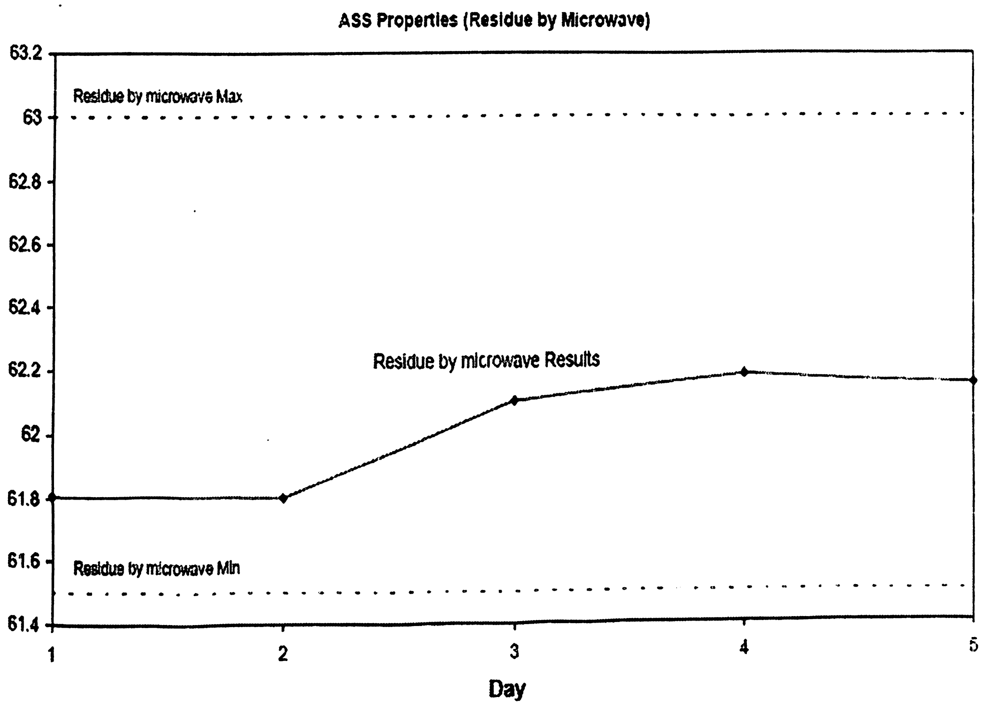
GRAPH 3: RESIDUE BY EVAPORATION FOR CRS



GRAPH 4: RESIDUE BY EVAPORATION FOR ASS

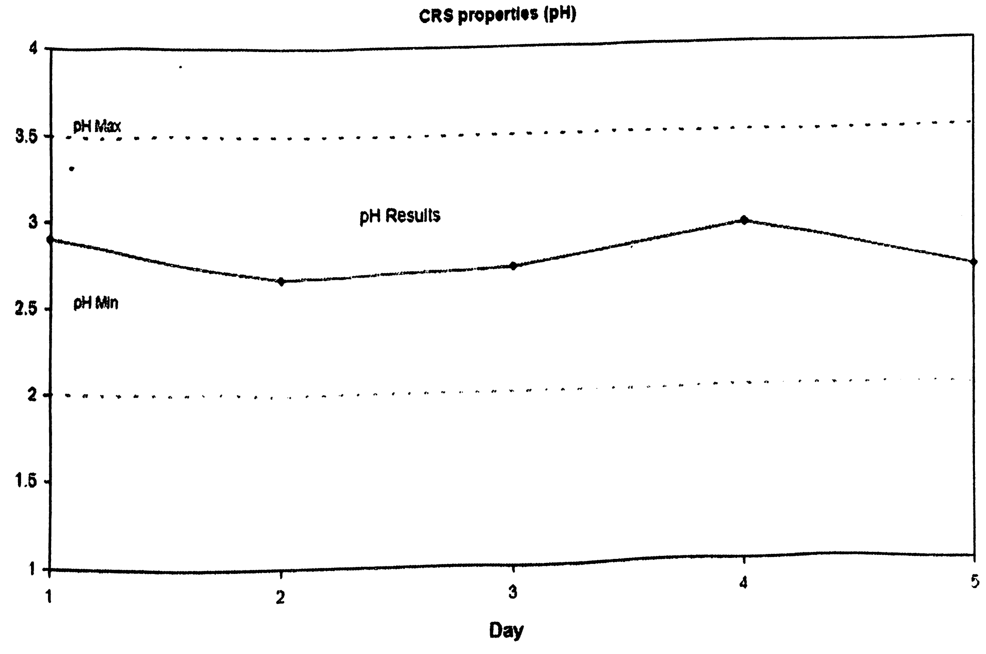


GRAPH 5: RESIDUE BY MICROWAVE FOR CRS

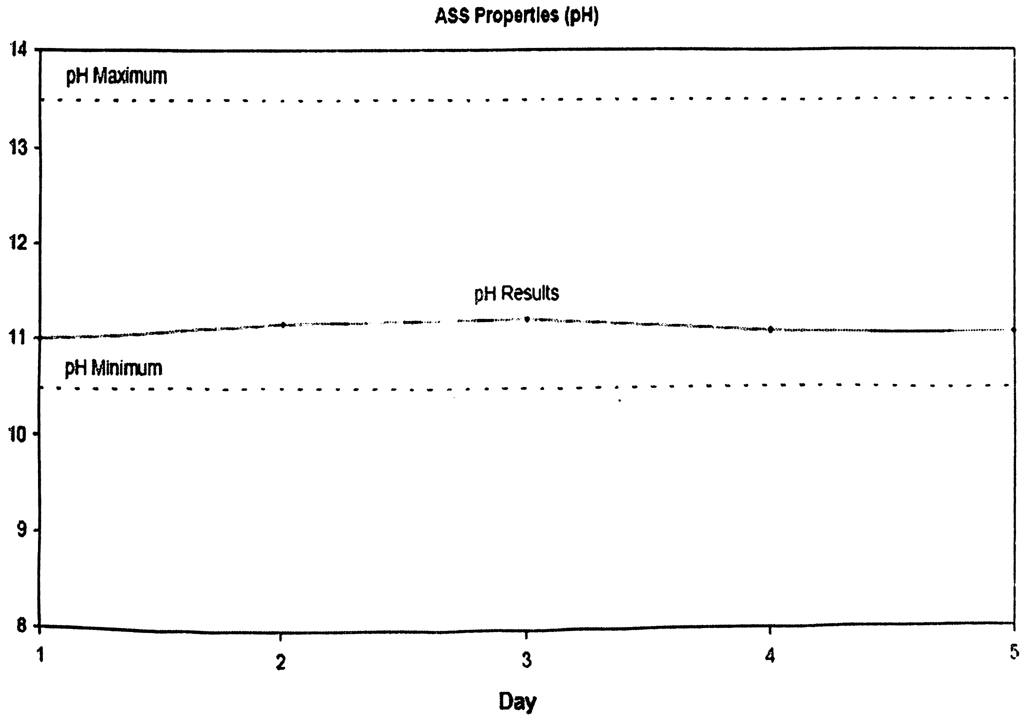


GRAPH 6: RESIDUE BY MICROWAVE FOR ASS

pH RESULTS



GRAPH 7: Ph VARIATIONS OF CATIONIC EMULSION



GRAPH 8: pH VARIATIONS OF ANIONIC EMULSIONS

OBSERVATIONS

By these experiments and the obtained results, it is clearly seen that the Anionic Slow Setting (ASS) emulsions have a constant pH variations, whereas for the cationic Rapid Setting (CRS) the pH value gives a disturbed variations each day.

The residue tests gave the declaration as the anionic emulsions are the one which meets its range between the upper and lower limit of the specification.

CONCLUSION

Thus the experimental results state that the Anionic Slow Setting Emulsions are more reliable than that of Cationic Rapid Setting Emulsions. However both are used in various applications where they meet their own specifications.

The Cationic Rapid Setting Emulsions can be improvised by changing it continuous phase or the dispersion medium by adding the Surface acting agents or Surfactants to the emulsion's continuous phase to compete its best with the Anionic Slow Setting Emulsions.

It also has provided me a future study on the stabilization of the Bitumen Emulsions, and how to enhance the stability of the frequently breaking or unstable Bitumen emulsions.

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APPENDIX I

CRS PROPERTIES

DAY	VISCOSITY	pH	RESIDUE BY EVAPORATION	RESIDUE BY MICROWAVE
1	65	2.9	60.25	60.61
2	65	2.67	60.49	61.01
3	64	2.74	60.69	61.12
4	63	2.97	60.70	61.02
5	62	2.69	60.95	60.93

APPENDIX II

ARS PROPERTIES

DAY	VISCOSITY	pH	RESIDUE BY EVAPORATION	RESIDUE BY MICROWAVE
1	80	11	61.31	61.80
2	80	11.2	61.30	61.8
3	79	11.2	61.37	62.1
4	78.5	11.1	61.40	62.18
5	76	11.1	61.50	62.15