Synthesis and Characterization of Surface Modified Nano-Silica for The Separation of Oil and Water

by

Shahrin bin Dzainal

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JULY 2009

Jniversiti Teknologi PETRONAS
andar Seri Iskandar
1750 Tronoh
erak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

04/11/09

AP Dr. Saikat Maitra)

Assoc. Prof Dr Saikat Maitra
Associate Professor
Cemical Engineering Departme
Universiti Teknologi PETRONAS

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JULY 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SHAHRIN BIN DZAINAL

ABSTRACT

Throughout this dissertation, the author presented the whole project in a form of a document for the future reference. This document is based on the research project entitled 'Synthesis and Characterization of Surface Modified Nano-Silica for the Separation of Oil and Water'. The project is basically on the preparation of surface modified silica in nano particle size to be use in oil-water separation. The effectiveness of the absorption will be proven by the characterization of the prepared substance. In the report, there will be 5 chapter; Introduction, Literature Review, Methodology, Results & Discussion and Conclusion & Recommendation. With the help of this report, it is hope that a better understanding gained regarding the research project.

ACKNOWLEDGEMENT

First and foremost, I would like to express my greatest gratefulness to the God for giving me the opportunity in completing my Final Year Project as per scheduled. He had shown me the guidance and help, and also given me the strength to overcome the problems while doing this research project.

I would also like to express my deepest thank and appreciation to my respective project Supervisor, AP Dr. Saikat Maitra for having faith in my credibility and ability on executing the assigned task. You have guided me so well in throughout this whole project. Your ongoing support is much appreciated. All that knowledge shared has really helped me to equip myself in being a better engineer in the future. Thanks also for being considerate in all decision that you have made for all this time.

Last but not list, thanks also to both supervisors, Dr. Anita Ramli and Dr Khalik M. Sabil for all the tolerance and advice given.

Thank you.

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CHAPTER 1

INTRODUCTION

1. BACKGROUND OF PROJECT

A serious problem which long has plagued industrial and environmental concern is the removal of hydrocarbons, particularly oil, from unwanted areas into or onto which it has been discharged. Of particular concerns is the removal of discharged oil from water or shore areas which occurs as a result, for example, of oil tankers accidents at sea or mishaps in the loading or unloading of oil from these tankers in port. Other occasions where hydrocarbon removal is of concern range from problems such as the discharge of oil at areas around oil wells and oil storage facilities or the cleaning of surfaces in which oil was stored (e.g. on-shore storage tanks, holds of tankers, etc.) to problems such as the discharge or leaking of oil from vehicles onto roads or driveway surfaces. Further, oil-water emulsions which are used, for example, as cutting fluids require separation of oil from the water prior to disposal.

Numerous solutions have been proposed for dealing with the problem of removing hydrocarbons from unwanted areas. One of these solutions involves the use of bacteria to degrade the hydrocarbons. However, such methods are expensive, raise important environmental concerns, and are often ineffective in cold weather environments.

Another solution to the problem lies in the use of absorbents which are intended to remove the hydrocarbons from unwanted areas by the use of physical forces rather than chemical break down of the hydrocarbons, i.e. where it is drawn into the absorbent material in much the same way water is drawn into a sponge. A lot of examples for absorbents of this type are found in the literature.

Some of the limitations of those examples mentioned include prohibitive cost; ineffectiveness in extreme environmental conditions; tackiness of the material after it is saturated with oil; retention of oil in the absorbent until the absorbent is removed from the water; and ineffective or temporary hydrophobic characteristics.

In order to effectively remove hydrocarbons from water it is necessary that the absorbent absorb only the hydrocarbon and not the water. That is, the material should be both oleophilic and hydrophobic. Fine particulate silica has been known to exhibit both of these properties. It can be treated to make it hydrophobic. But, upon standing in water for a number of hours, the silica loses its hydrophobicity, becomes hydrophilic, enters the water, leaving the oil floating on top.

Another problem is that after treated silica is exposed to and has absorbed the hydrocarbons, the material does not agglomerate. Thus, it is difficult, if not impossible, to recover the saturated material without the use of very fine mesh screens.

2. PROBLEM STATEMENT

The separation of oil and water is highly demanded right now as there are many areas involved with this matter. Areas such as oil and gas industry, oil pollution problem and water treatment system need a very effective oil and water separation technique to save money and time. It is true that there are quite a number of existed conventional methods, but the effectiveness of those methods is a bigger disappointment.

Therefore, there is a need of finding a new method to enhance the existed method, which is more effective and reliable. Through the researches being done, there are a few methods that can be improved and the most promising one is the separation process using nano-silica. The improvement of this method is depending greatly on the betterment of the properties of nano-silica particle that is used in the separation process.

It has been theoretically studied that the efficiency of nano-silica can be simply improved by its surface modification with selected hydrophobic organic molecules in the specific processes. With respect to that, the author has been decided on proving those theoretical studies and finding the best organic molecules which led to that improved nano-silica in the course of lab experimentation.

3. OBJECTIVES & SCOPE OF STUDY

- Self-prepared the surface modified nano-silica using a new experimental method.
- Characterized the finished product using a few equipments available.

For the scope of study, the author will synthesized the surface modified nano-silica with the selected hydrophobic substances. The characterization process of the nano-silica will then take place.

CHAPTER 2

LITERATURE REVIEW

1. SEPARATION OF OIL AND WATER

In order to separate oil from water, it is necessary to understand first about the structure and the properties of both two substances. The separation process maybe looks quite simple as oil and water are different in term of their density. But in the real situation, this process requires more than just a difference in density to achieve the best result. Other properties also have to be considered and most importantly are the effect of the structure of each of the substances to the process. Therefore the better understanding in the structure and properties of oil and water will help a lot in reaching this project objective.

As the basis of the project, fine particle size treated hydrophobic silica is added to water which contains oil. The silica sorbs the oil and the silica/oil mixture floats on top of the water where it can be scooped off or otherwise substantially separated from the water. The oil and silica may then be conveniently separated by placed back into water and allowed to stand for an extended period of time until the silica loses its hydrophobicity, becomes hydrophilic, and goes into the water phase leaving the oil floating on the water. The oil may then be removed for further handling and the silica may then be separated from the water for further handling.

The expression "oil" is meant to include liquid hydrocarbons, e.g. gasoline, kerosene, fuel oil, crude oil, paraffinic oils, vegetable oils, and the like and includes such water-immiscible liquids as xylene, toluene, styrene, alkylbenzenes, naphta, naphthenic compounds, liquid organic polymers, and the like.

The water, which contains the oil desired to be separated, may be a river, lake, effluent ditch, bay, holding tank or process stream. Waters containing dissolved ingredients and saline waters, e.g., brines, seawater, estuaries, and the like are also can be considered.

The ratio of oil to water is not particularly significant except that there should be enough of one with the other to be considered as being something more than "insignificant" for the present invention to be economically practical. In instance where there is a relatively small amount of water to oil, a water phase may form at the bottom; this water layer may be drawn off, generally along with a small amount of the oil, and then the so-removed water layer may be treated to remove any oil which may have been drawn off the water. Usually, however, the oil desired to be separated from water involves a relatively small amount of oil in a large amount of water.

In most instances, it is desired to remove as much oil from the water as is reasonably possible; in these cases some water may be taken along with the silica/oil mixture. This is not generally a problem because the convenient manner of separating the oil from the silica involves adding enough water so that it will take up the silica when the silica reverts from hydrophobic to hydrophilic, allowing the oil to remain floating on top of the water.

1.1 Water

Water (H_2O) is often perceived to be ordinary as it is transparent, odourless, tasteless and ubiquitous. It is the simplest compound of the two most common reactive elements, consisting of just two hydrogen atoms attached to a single oxygen atom. Indeed, very few molecules are smaller or lighter. Liquid water, however, is the most extraordinary substance. Liquid water has importance as a solvent, a solute, a reactant and a biomolecule, structuring proteins, nucleic acids and cells and controlling our consciousness. H_2O is the second most common molecule in the Universe (behind hydrogen, H_2), the most abundant solid material and fundamental to star formation.

Many of the physical and chemical properties of water are due to its structure. The atoms in the water molecule are arranged with the two H-O bonds at an angle of about 105° rather than on directly opposite sides of the oxygen atom. The asymmetrical shape of the molecule arises from a tendency of the four electron pairs in the valence shell of oxygen to arrange themselves symmetrically at the vertices of a tetrahedron around the oxygen nucleus. The two pairs associated with covalent bonds holding the hydrogen atoms are drawn together slightly, resulting in the angle of 105° between these bonds.

This arrangement results in a polar molecule, since there is a net negative charge toward the oxygen end (the apex) of the V-shaped molecule and a net positive charge at the hydrogen end. The electric dipole gives rise to attractions between neighboring opposite ends of water molecules, thus enabling each of the oxygen to attract two nearby hydrogen atoms of two other water molecules. Such hydrogen bonding, as it is called, has also been observed in other hydrogen compounds. Although considerably weaker than the covalent bonds holding the water molecule together, hydrogen bonding is strong enough to keep water liquid at ordinary temperatures; its low molecular weight would normally tend to make it a gas at such temperatures.

Various other properties of water, such as its high specific heat, are due to these hydrogen bonds. As the temperature of water are lowered, clusters of molecules form through hydrogen bonding, with each molecule being linked to others by up to four hydrogen bonds, each oxygen atom tends to surround itself with four hydrogen atoms in a tetrahedral arrangement. Hexagonal rings of oxygen atoms are formed in this way, with alternate atoms in either a higher or lower plane than their neighbors to create a kinked three-dimensional structure.

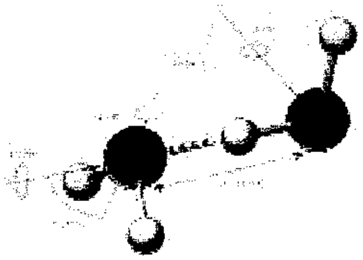


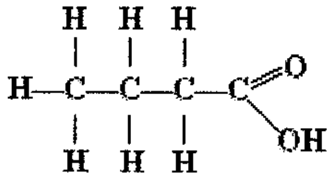
Figure 1: The molecular structure of water

1.2 Oil

Lipids consist of numerous fatlike chemical compounds that are insoluble in water but soluble in organic solvents. Lipid compounds include monoglycerides, diglycerides, triglycerides, phosphatides, cerebrosides, sterols, terpenes, fatty alcohols, and fatty acids. Dietary fats supply energy, carry fat-soluble vitamins (A, D, E, K), and are a source of antioxidants and bioactive compounds. Fats are also incorporated as structural components of the brain and cell membranes.

Fatty acids consist of the elements carbon (C), hydrogen (H) and oxygen (O) arranged as a carbon chain skeleton with a carboxyl group (-COOH) at one end. Saturated fatty acids (SFAs) have all the hydrogen that the carbon atoms can hold, and therefore, have no double bonds between the carbons.

Monounsaturated fatty acids (MUFAs) have only one double bond. Polyunsaturated fatty acids (PUFAs) have more than one double bond.



Butyric Acid

Butyric acid (butanoic acid) is one of the saturated short-chain fatty acids responsible for the characteristic flavor of butter. This image is a detailed structural formula explicitly showing four bonds for every carbon atom and can also be represented as the equivalent line formulas:

$CH_3CH_2CH_2COOH$ or $CH_3(CH_2)_2COOH$

The numbers at the beginning of the scientific names indicate the locations of the double bonds. By convention, the carbon of the carboxyl group is carbon number one. Greek numeric prefixes such as *di, tri, tetra, penta, hexa,* etc., are used as multipliers and to describe the length of carbon chains containing more than four atoms. Thus, "9, 12-octadecadienoic acid" indicates that there is an 18-carbon chain (octa deca) with two double bonds (di en) located at carbons 9 and 12, with carbon 1 constituting a carboxyl group (oic acid). The structural formula corresponds to:

$CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$

9, 12-octadecadienoic acid (Linoleic Acid)

This would be abbreviated as:

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Fatty acids are frequently represented by a notation such as C18:2 that indicate that the fatty acid consists of an 18-carbon chain and 2 double bonds. Although this could refer to any of several possible fatty acid isomers with this chemical composition, it implies the naturally-occurring fatty acid with these characteristics, i.e., linoleic acid. Double bonds are said to be "conjugated" when they are separated from each other by one single bond, e.g., (-CH=CH-CH=CH-). The term "conjugated linoleic acid" (CLA) refers to several C18:2 linoleic acid variants such as 9, 11-CLA and 10, 12-CLA which correspond to 9, 11-octadecadienoic acid and 10, 12-octadecadienoic acid. The principal dietary isomer of CLA is *cis*-9, *trans*-11 CLA, also known as rumenic acid. CLA is found naturally in meats, eggs, cheese, milk and yogurt.

$CH_3(CH_2)_5CH{=}CH{-}CH{=}CH(CH_2)_7COOH$

9, 11-Conjugated Linoleic Acid

1.3 Hydrophobic Effect

The hydrophobic effect is the property that non-polar molecules tend to form intermolecular aggregates in aqueous medium and analogous intramolecular interactions. The name arises from the combination of water in Attic Greek *hydro-* and for fear *phobos*, which describes the apparent repulsion between water and hydrocarbons. At the macroscopic level, the hydrophobic effect is apparent when oil and water are mixed together and form separate layers or the beading of water on hydrophobic surfaces such as waxy leafs.

At the molecular level, the hydrophobic effect is an important driving force for biological structures and responsible for protein folding, protein-protein interactions, formation of lipid bilayer membranes, nucleic acid structures, and protein-small molecule interactions. According to the solvophobic theory of Reversed Phase Chromatography (RPC), the hydrophobic effect is driven by the loss of hydrogen bonding and the higher entropic cost of forming a cavity around nonpolar molecules. These losses can be minimized by forcing nonpolar molecules together.

1.4 Oleophilic Effect

The oleophilic effect is actually the properties of a substance where it has a tendency to absorb oil more than water. Based on the above findings, the best substance to be used in the water treatment process should consist of both the hydrophobic and also the oleophilic behavior to attain effective separation of oil and water.

2. SURFACE MODIFIED NANO-SILICA

Surface modified nano-silica is basically the ordinary silica in nano particle size which has undergoes the synthesized process with hydrophobic organic molecules. With this synthesized process which is the grafting of the nano-silica, the hydrophobicity characteristics will be achieved. As has been stated earlier on, this hydrophobicity together with oleophilicity is two characteristics that crucial in developing more effective absorbent material.

Nano-silica is quite promising in being the absorbent material for the separation of oil and water. However the major improvement of the substance can only be done to its surface properties which tell the reason of the author choosing the grafting method for the modification purposed. The grafting method is also low in cost and not really complicated like any other existed methods.

2.1 Silica

Silica or silicon dioxide (from the Latin *silex*), is an oxide of silicon with a chemical formula of SiO_2 and has been known for its hardness since antiquity. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. It is a principal component of most types of glass and substances such as concrete. Silica is the most abundant mineral in the earth's crust.

SiO_2 has a number of distinct crystalline forms in addition to amorphous forms. With the exception of stishovite and fibrous silica, all of the crystalline forms involve tetrahedral SiO_4 units linked together by shared vertices in different arrangements. Silicon-oxygen bond lengths vary between the different crystal forms, for example in α-quartz the bond length is 161 pm, whereas in α-tridymite it is in the range 154-171 pm. The Si-O-Si angle also varies between low values of 140° in α-tridymite, up to 180° in β-tridymite. In α-quartz the Si-O-Si angle is 144°.

Fibrous sulfur has a structure similar to that of SiS_2 with chains of edge-sharing SiO_4 tetrahedra. Stishovite, the highest pressure form, in contrast has a rutile like structure where silicon is 6 coordinate. The density of stishovite is 4.287 g/cm^3, which compares to α-quartz, the densest of the low pressure forms, which has a density of 2.648 g/cm^3. The difference in density can be ascribed to the increase in coordination as the six shortest Si-O bond lengths in stishovite (four Si-O bond lengths of 176 pm and two others of 181 pm) are greater than the Si-O bond length (161 pm) in α-quartz. The change in the coordination increases the ionicity of the Si-O bond. Note that the only stable form under normal conditions is α-quartz and this is the form in which crystalline silicon dioxide is usually encountered. In nature impurities in crystalline α-quartz can give rise to colours.

Nano-silica is quite promising in being the absorbent material for the separating of oil from water, with the major improvement of the substance can only be done to its surface. There are a few methods to perform these improvements such as the hydrophobic coating and the grafting process.

Sand consists of small grains or particles of mineral and rock fragments. Although these grains may be of any mineral composition, the dominant component of sand is the mineral quartz, which is composed of silica. Other components may include aluminium, feldspar and iron-bearing minerals. Sand with particularly high silica levels that is used for purposes other than construction is referred to as silica sand or industrial sand.

For a particular source of sand to be suitable for glassmaking, it must not only contain a very high proportion of silica but also should not contain more than strictly limited amounts of certain metallic elements. Silica sand is also normally required to be well-sorted, i.e. to have grains of an approximately uniform size. Most sources of sand used by the construction industry do not satisfy these requirements and are not, therefore, suitable for glassmaking. Industrial uses of silica sand depend on its purity and physical characteristics. Some of the more important physical properties are: grain size and distribution, grain shape, sphericity, grain strength and refractoriness.

2.2 Hydrophobic Coating

Hydrophobic coatings, and in particular super hydrophobic coatings, have many uses. It is used to render surfaces water proof or water resistant. Superhydrophobic coatings have a "self-cleaning" property as dirt, bacteria, spores or other substances that come into contact with the surface cannot readily adhere to the coating and are readily washed off by water.

Prior art methods of forming super hydrophobic coatings on the surface of a substrate typically use a significant amount of organic solvents. The use of such solvents is undesirable as such solvents have adverse environmental effects, and are often toxic and flammable and therefore need to be handled with care. Superhydrophobic coatings are generally opaque. This is because the hydrophobicity of such coatings is due to both the chemical of the surface of the coating and the rough surface structure of the coating. Rough surfaces tend to scatter light which causes the surface of the coating to appear opaque.

2.3 Grafting Process

Grafting process is the other alternative in developing the super hydrophobic surface on the wanted substances. Compared to other methods, this process is considered to be less complex and low in cost. Thus, it quite a suitable process in producing the super hydrophobic silica since the maintenance cost will be small and the raw material cost can be reduced.

This process is basically focusing on modifying the surface structure of the silica through some synthesizing phase. The silica will be synthesized with the chosen hydrophobic organic component where in the end the silica shall embody the hydrophobic characteristic of that organic component.

CHAPTER 3

METHODOLOGY

1. PROJECT IDENTIFICATION

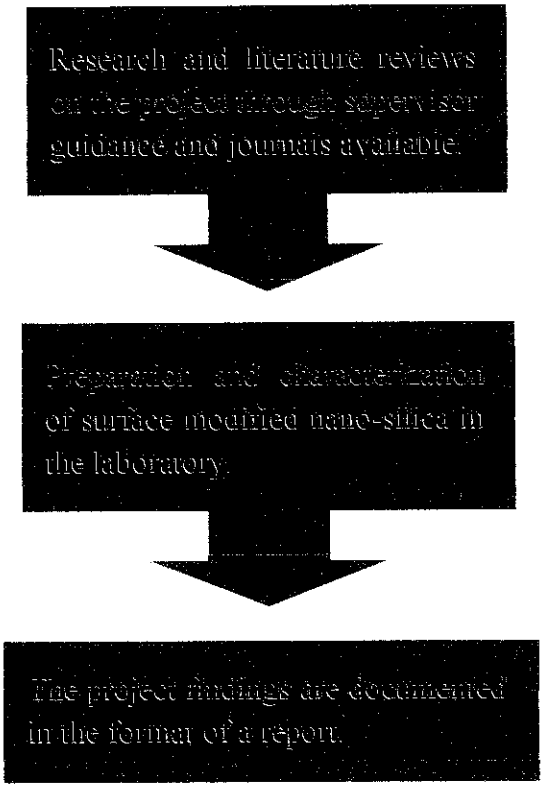
In the proposed project, nano-silica will be generated by chemical treatment with locally available siliceous materials. The synthesis process has to be standardized with respect to nature of chemicals used, reaction time, temperature etc. The materials then will be characterized thoroughly.

The synthesized process is going to be done to nano-silica by the application of hydrophobic organic molecules. This process is called the grafting process. Theoretically, the process will result in nano-silica which employs the hydrophobic characteristic. Different types of organic molecules are going to be used in the process, in order to find the best molecules that will make the nano-silica most hydrophobic.

After the surface modified nano-silica is already prepared, it will then be characterized to know its properties. The characterization process is done with some equipment available such as FTIR, XRD, SEM and TGA.

2. FLOW CHART

Below is the overview of the process procedures which is taken during the completion of the whole project.



3. CHEMICAL REACTION

Here are the chemical reactions available to be used in the process.

3.1 Treatment with Sodium Carbonate

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

$$Na_2SiO_3 + HCl \rightarrow H_2SiO_3 + NaCl$$

3.2 Treatment with Sodium Hydroxide

$$NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

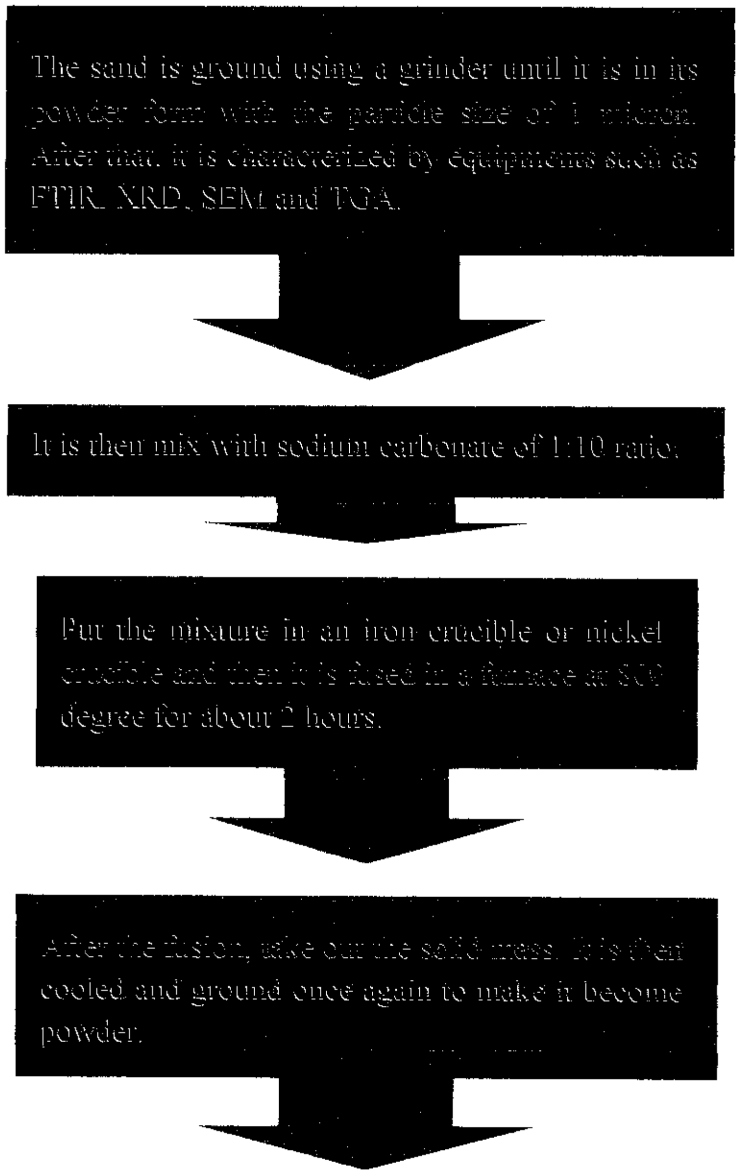
$$Na_2SiO_3 + HCl \rightarrow H_2SiO_3 + NaCl$$

At the end of the both treatments, the amorphous silica is formed.

4. PREPARATION OF NANO-SILICA

In preparing the surface modified nano-silica, this project has resolved in using two slightly different approach based on the treatment and equipments available. First one is approach by using teflon beaker and the second is by using teflon crucible.

4.1 Iron or Nickel Crucible (Sodium Carbonate Treatment)

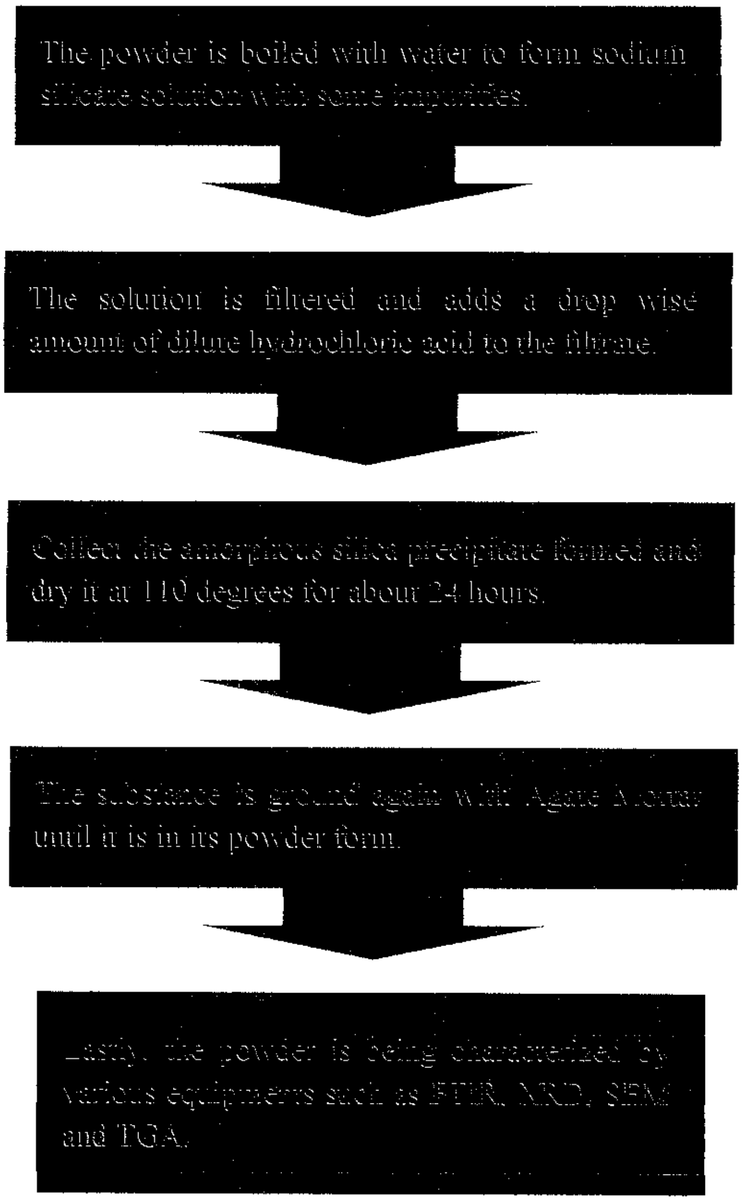


The sand is ground using a grinder until it is in its powder form with the particle size of 1 micron. After that, it is characterized by equipments such as FTIR, XRD, SEM and TGA.

It is then mix with sodium carbonate of 1:10 ratio.

Put the mixture in an iron crucible or nickel crucible and then it is fused in a furnace at 800 degree for about 2 hours.

After the fusion, take out the solid mass. It is then cooled and ground once again to make it become powder.



The powder is boiled with water to form sodium silicate solution with some impurities.

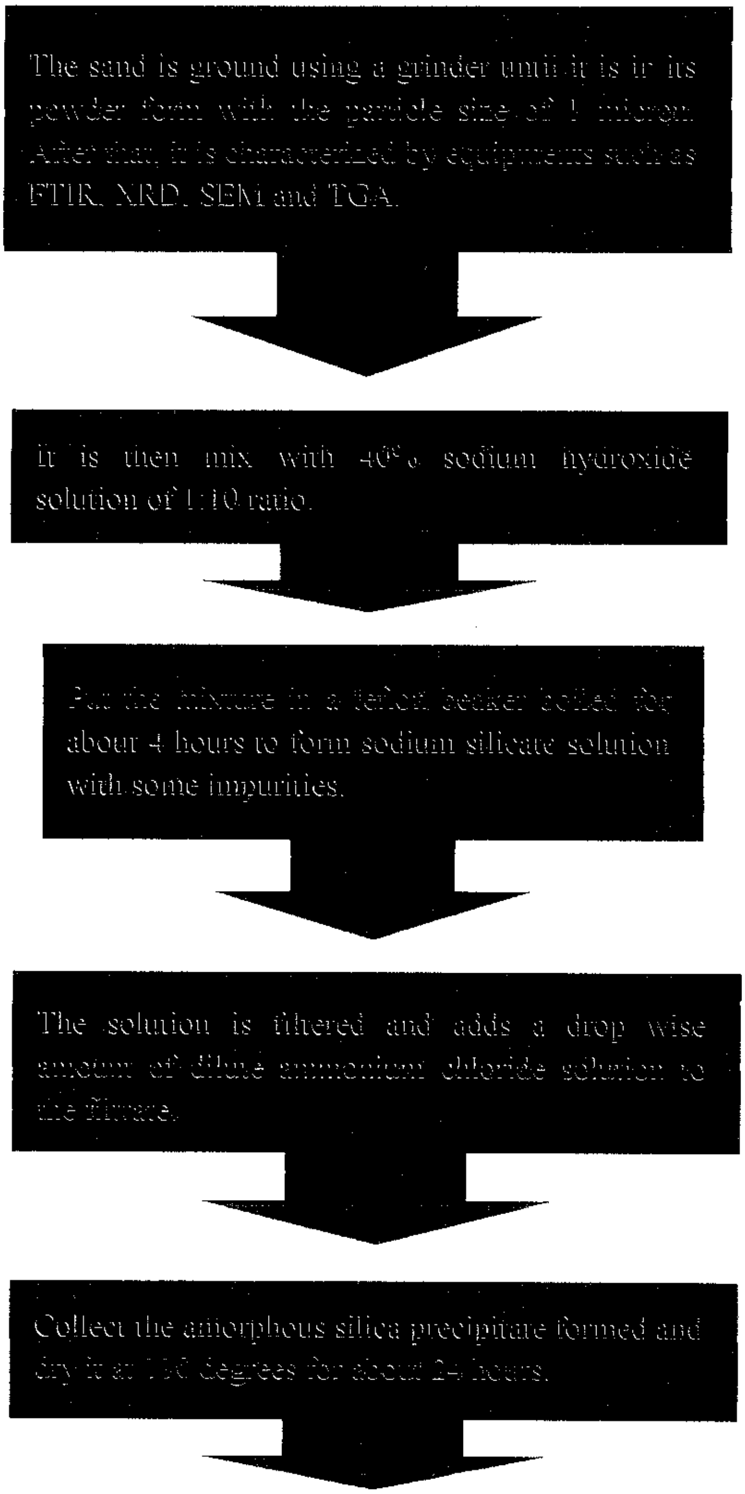
The solution is filtered and adds a drop wise amount of dilute hydrochloric acid to the filtrate.

Collect the amorphous silica precipitate formed and dry it at 110 degrees for about 24 hours.

The substance is ground again with Agate Mortar until it is in its powder form.

Lastly, the powder is being characterized by various equipments such as FTIR, XRD, SEM and TGA.

4.2 Teflon Beaker (Sodium Hydroxide Treatment)



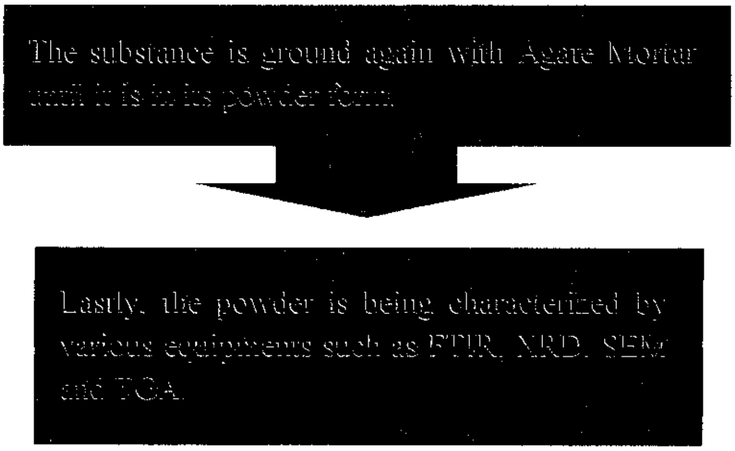
The sand is ground using a grinder until it is in its powder form with the particle size of 1 micron. After that, it is characterized by equipments such as FTIR, XRD, SEM and TGA.

It is then mix with 40% sodium hydroxide solution of 1:10 ratio.

Put the mixture in a teflon beaker boiled for about 4 hours to form sodium silicate solution with some impurities.

The solution is filtered and adds a drop wise amount of dilute ammonium chloride solution to the filtrate.

Collect the amorphous silica precipitate formed and dry it at 150 degrees for about 24 hours.



The substance is ground again with Agate Mortar until it is in its powder form.

Lastly, the powder is being characterized by various equipments such as FTIR, XRD, SEM and TGA.

5. CHEMICALS AND EQUIPMENTS

Here is the list of chemicals and equipments involved during the project work.

5.1 Chemicals

- Sodium carbonate
- 40% sodium hydroxide solution
- Dilute hydrochloric acid
- Dilute ammonium chloride solution

5.2 Equipments

- Iron crucible
- Nickel crucible
- Grinder
- Hot plate
- Glass beaker

- Filter
- Furnace
- Stirrer
- Oven

CHAPTER 4

RESULTS & DISCUSSION

1. RESULTS

As there are 2 available characterization equipments, the results consist of FTIR and XRD analysis only.

1.1 FTIR

FTIR characterization on the sand being used in the project before the synthesis process began.

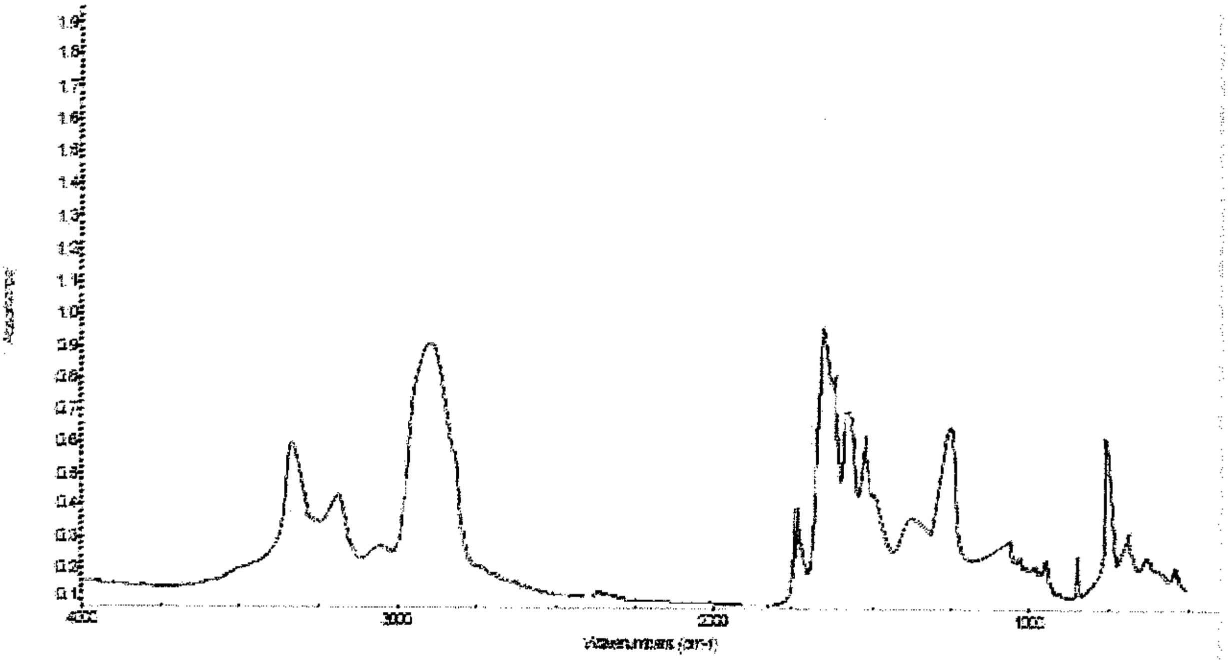


Figure 1: Plot from FTIR

FTIR characterization on the prepared substance after the synthesis process takes place.

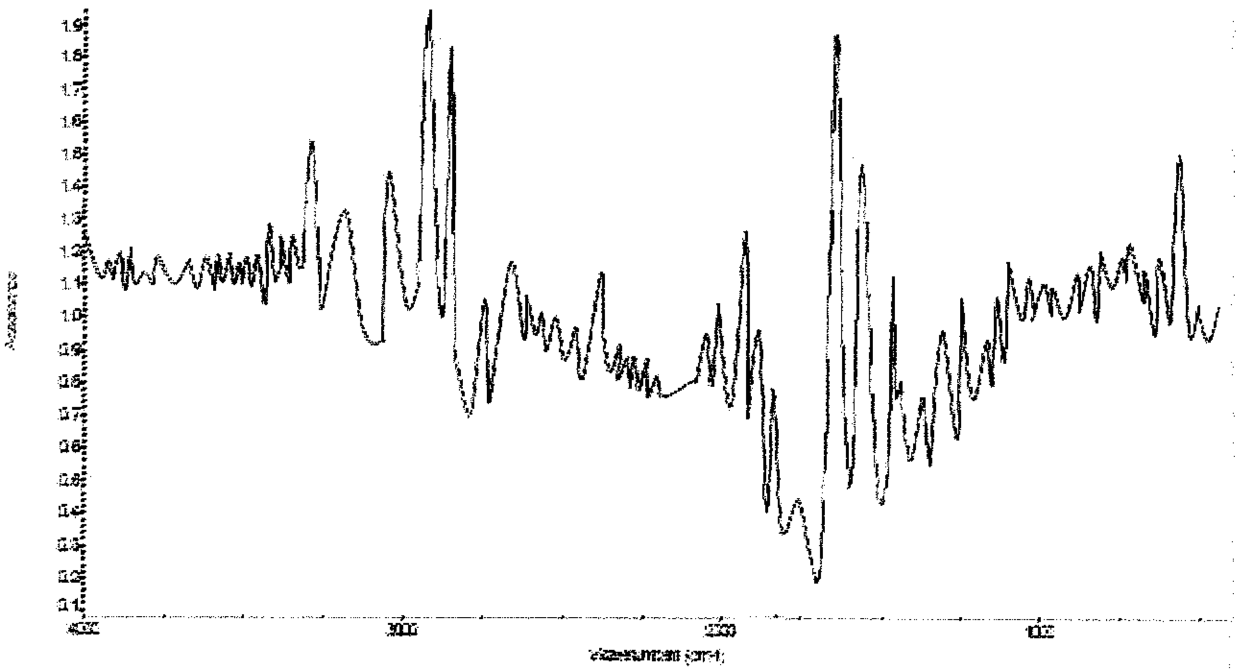


Figure 2: Plot from FTIR

1.2 XRD

XRD characterization on the sand being used in the project before the synthesis process began.

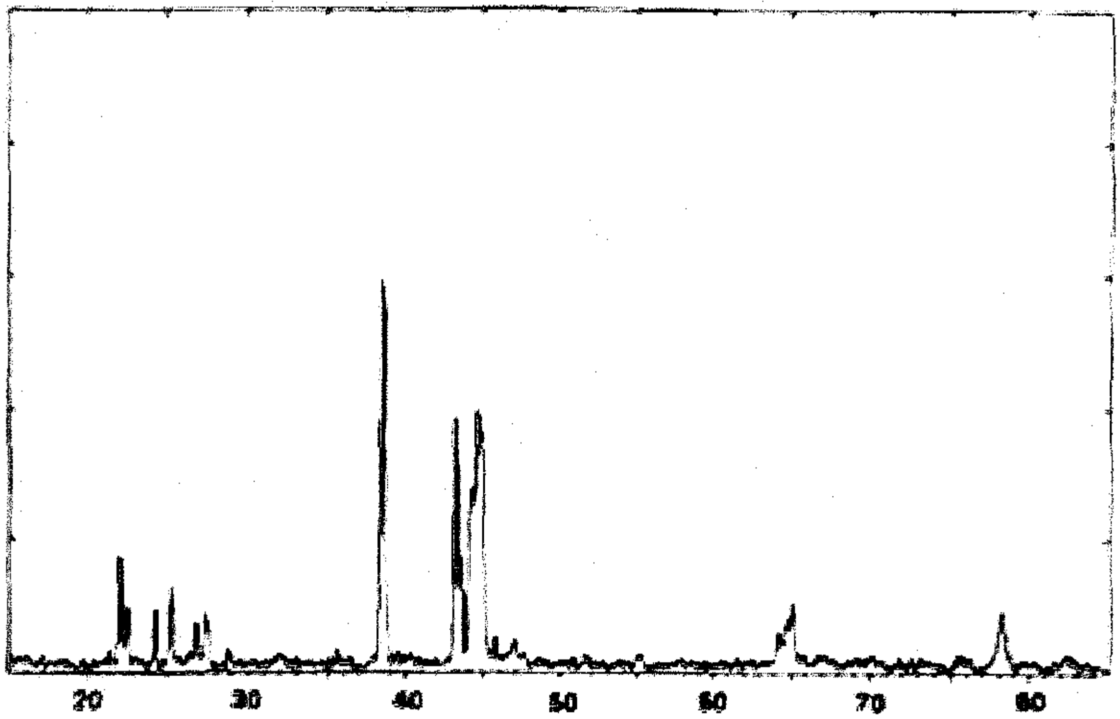


Figure 3: Plot from XRD

XRD characterization on the prepared substance after the synthesis process takes place.

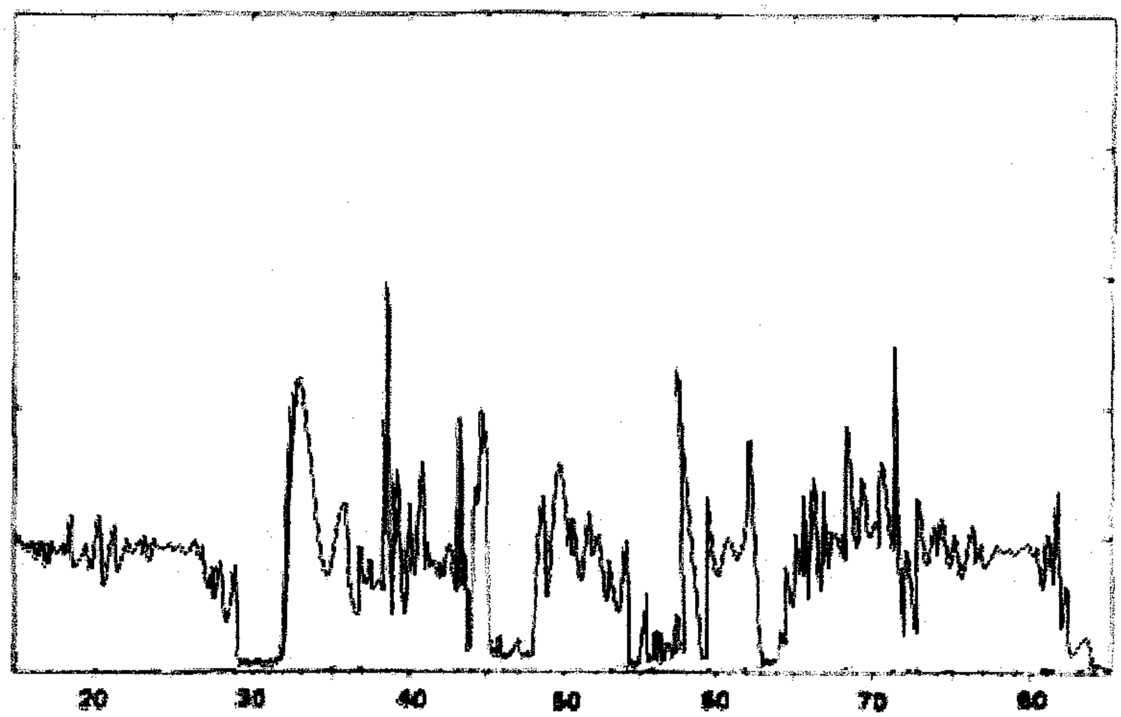


Figure 4: Plot from XRD

1.3 Yield Percent

- Sodium carbonate treatment

For this treatment the predicted values to be produced is 5g and the actual produced values is 3.5g. Thus,

$$\text{Yield } \% = (3.5/5)*100$$

$$= 70\%$$

- Sodium hydroxide treatment

  For this treatment the predicted values to be produced is 4g and the actual produced values is 3g. Thus,

$$\text{Yield \%} = (3/4)*100$$

$$= 75\%$$

2. DISCUSSION

2.1 FTIR

The FTIR will basically detect the vibration characteristics of silica groups in the sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, the silica group will absorb the infrared radiation and resulted in the emerging of the peaks in the plot. The characterization of the sand is being done to ensure the existence of the silica component in the sand. It is done before the process began to prove that there are silica particle in sand. It is important since only with its existence, the project will then continued. From the plot as shown in figure 1, it can be seen that a few peaks emerged which indicate that the sand used do contained silica particle but in a small amount. After being synthesis it can be seen that more peaks with higher values developed in figure 2. Thus it is proven that the produced substance does have a large amount of silica particle.

2.2 XRD

Every crystalline substance produced its own XRD pattern, which because it is dependent on the internal structure, which is the characteristic of a specific substance. Using the XRD, the concentration or amount of a component can detected using the X-ray to diffract the internal structure of the component in all possible orientations. The concentration is shown by the peaks emerged in the plot. Same as the characterization using FTIR, the function of XRD is also to prove the existence of silica particle in the sand and substance produced. From the plot in figure 3, it is shown that the amount of silica component which exists in the sand used is low as there are only few peaks in the plot. However, after the synthesis process is being done, figure 4 shows that the concentration of silica particle is higher relative to the high values peaks emerged.

2.3 Methods' Comparison

From the observation done throughout the laboratory experiment, it has been identified that the synthesis of surface modified nano-silica using the sodium hydroxide treatment is more favorable. This is because the substance produced from both treatments is basically the same and the amount is almost the same as from the yield percentage calculation. However the treatment with sodium hydroxide is simpler compared to the treatment with sodium carbonate. Since this project also wants to find the less complex method in the synthesis of surface modified nano-silica, it is recommended to use the sodium hydroxide treatment.

CHAPTER 5

CONCLUSION & RECOMMENDATION

1. CONCLUSION

To conclude this report, it is best to say that the objectives of the project are successfully achieved although there are quite a few of obstacles that have to be faced. Despite all of the problems, the project has been able to carry through and finished in the given period of time.

Based on the results and discussions for this project, it has proved that the synthesis process choose for the silica is able to produce a chemical substance which contained a considerably high amount of surface modified nano-silica particle. Thus, with further improvement and innovation, it is believe that the project will be a major impact to the industry.

REFERENCES

Xiaohong Li, Zhi Cao, Feng Liu, Zhijun Zhang, and Hongxin Dang, 2005, "A Novel Method of Preparation of Superhydrophobic Nano-silica in Aqueous Solution".

James F. Warrenchak, and Edward F. Phelan, 1991. *Treated Silica for Oil Absorption.* Patent no. 5037557, New York, USA

Donald W. Calvin, 1979. *Removing Oil from Water.* Patent no. 4151078, USA

Donald W. Calvin, 1977. *Method of Preparing Hydrophobic Silica.* Patent no. 4054689, USA

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APPENDICES

United States Patent [19]
Calvin

[11] **4,151,078**
[45] **Apr. 24, 1979**

[54] REMOVING OIL FROM WATER

[75] Inventor: **Donald W. Calvin**, Zachary, La.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **824,003**

[22] Filed: **Aug. 12, 1977**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 730,556, Oct. 7, 1976, abandoned.

[51] **Int. Cl.**^{2} **C02B 9/02**
[52] **U.S. Cl.** .... **210/30 A**; 210/36; 210/40; 210/DIG. 26
[58] **Field of Search** .... 210/30 A, 40, DIG. 26, 210/36, 242 AS, 502; 423/336, 337, 335

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,535,036	12/1950	Broughton	423/336
3,203,759	8/1965	Flemmert	423/337
3,484,371	12/1969	Biegler et al.	210/DIG. 26
3,562,153	2/1971	Tully et al.	210/DIG. 26
3,752,762	8/1973	Cincotta	210/DIG. 26

FOREIGN PATENT DOCUMENTS

47-15026	5/1972	Japan	210/40

Primary Examiner—Charles N. Hart
Assistant Examiner—Ivars Cintins
Attorney, Agent, or Firm—W. J. Lee

[57] ABSTRACT

Hydrophobic silica, containing sorbed HF values, is used to remove oil from water by sorption of the oil onto the silica and then separating the oil/silica mixture from the water. Furthermore, the present invention pertains to recovering the silica from the oil by aqueous treatment in such a manner that the hydrophobicity of the silica is overcome and the silica becomes hydrophilic, thereby releasing the oil.

4 Claims, No Drawings

REMOVING OIL FROM WATER

This application is a continuation-in-part of Ser. No. 730,556 filed Oct. 7, 1976, now abandoned.

CROSS-REFERENCE TO RELATED APPLICATIONS

In my co-filed application, Ser. No. 730,541 filed Oct. 7, 1976 titled "Method of Preparing Hydrophobic Silica", now U.S. Pat. No. 4,054,689, it is shown that fine-particle silica may be rendered hydrophobic by being treated with anhyrous gaseous HF, thereby sorbing HF values onto the silica. This said co-filed application is incorporated herein by reference.

BACKGROUND OF THE INVENTION

There have been numerous attempts to find efficient, economical methods for removing oil from water, especially when the oil appears to be environmentally or ecologically detrimental. Adside from the possible danger to animal life, plant life, or marine life, oil in waterways can be a fire hazard, can present chemical problems to segments of the public or industry who may use the water in various processes, and can be wasteful and a general nuisance. In some cases, exotic or expensive oils need to be saved from loss.

Among the many methods which have been taught and proposed for removing oil from water have been the use of various sorption agents or sorptives, such as wood chips, sawdust, sulfur, polymeric substances, cellulosic substances, and many others. Many of the proposed sorptives are not salvageable or re-usable and are intended to be destroyed or discarded along with the sorbed oil. In some cases, it is possible to recover a fair amount of the oil from the sorptive by draining, squeezing, or washing with a solvent. Even when some of the oil is recovered from the sorptive, the sorptive along with residual oil is generally intended to be discarded or destroyed.

There exists a need for a sorption agent (sorptive) from which the sorbed oil can be easily removed and which is further useful.

It is an object of the present invention to provide a sorptive for removal of oil from water.

It is a further object to provide a sorptive from which the oil can be substantially completely recovered.

A still further object is to provide a sorptive which is again useful after the oil has been removed.

Yet another object is to provide a sorptive which can be treated so as to render it useful again as a sorptive for removing oil from water.

These and other objects are attained by the present invention as described herein.

SUMMARY OF THE INVENTION

Fine particle size silica which contains sorbed HF values and which is hydrophobic is brought into contact with a mixture of oil and water. The oil becomes sorbed on the silica and the oil-laden silica is removed from the water.

The oil-laden hydrophobic silica may then be treated with water for a period of time sufficient to overcome the hydrophobicity of the silica, and when it becomes hydrophilic by losing its hydrophobicity, it goes into the water and allows the oil to remain on the surface of the water where it can be recovered.

The silica, now hydrophilic, may be separated from the water and put to further use or it may be treated to render it hydrophobic again.

DETAILED DESCRIPTION OF THE INVENTION

Fine particle size hydrophobic silica (SiO_2) containing sorbed HF values is added to water which contains oil. The silica sorbs the oil and the silica/oil mixture floats on top of the water where it can be scooped off or otherwise substantially separated from the water. The oil and silica may then be conveniently separated by being placed back into water and allowed to stand for an extended period of time until the silica loses its hydrophobicity, becomes hydrophilic, and goes into the water phase leaving the oil floating on the water. The oil may then be removed for further handling and the silica may then be separated from the water for further handling.

Throughout this disclosure, the expression "oil" is meant to include liquid hydrocarbons, e.g. gasoline, kerosene, fuel oil, crude oil, paraffinic oils, vegetable oils, and the like and also includes such water-immiscible liquids as xylene, toluene, styrene, alkylbenzenes, naphtha, naphthenic compounds, liquid organic polymers, and the like.

The water, which contains the oil desired to be separated, may be a river, lake, effluent ditch, bay, holding tank or process stream. Waters containing dissolved ingredients and saline waters, e.g., brines, seawater, estuaries, and the like are within the purview of the present invention.

The ratio of oil to water is not particularly significant except that there should be enough of one with the other to be considered as being something more than "insignificant" for the present invention to be economically practical. In instances where there is a relatively small amount of water to oil, a water phase may form at the bottom; this water layer may be drawn off, generally along with a small amount of the oil, and then the so-removed water layer may be treated according to the present invention to remove any oil which may have been drawn off the water. Usually, however, the oil desired to be separated from water involves a relatively small amount of oil in a large amount of water.

In most instances, it is desired to remove as much oil from the water as is reasonably possible; in these cases some water may be taken along with the silica/oil mixture. In the present invention this is not generally a problem because the convenient manner of separating the oil from the silica involves adding enough water so that it will take up the silica when the silica reverts from hydrophobic to hydrophilic, allowing the oil to remain floating on top of the water in the separation apparatus.

The process may be operated batchwise, continuously, intermittently, or by continuous batching. A number of separative steps may be employed and the final water phase, which may still contain very small amounts of oil, may be re-cycled back to a preceeding step or may be passed to further processing.

In certain batch operations or sporadic operations the number of steps, and the completeness of the separation of oil and water, is done in accordance with whether one wishes substantially water-free oil or oil-free water as the main result. It is recognized by practitioners of the relevant arts that oil and water tend to form two distinct phases and that if all the oil, even that at the phase interface, is to be drained or siphoned off the water, then some of the water may accompany the oil. Conversely, if all the water is to be drained from beneath the oil, then some of the oil at the interface may accompany the water. Either the water phase or the oil phase may be recycled back into the separation process, if desired, after a phase separation step. The silica in the water phase is ordinarily substantially removed for further processing, even though some or all of it may remain with the recycle water, if desired.

In continuous batching (or continuous "tandem") operations the oil/water mixture is treated with the hydrophobic silica thereby forming a silica/oil mixture which floats on the water. The silica/oil mixture is scooped off, vacuumed off, weired, or otherwise removed, and then mixed in a separate reservoir with water where, after a period of time, the hydrophobic silica becomes hydrophilic and goes into the water phase leaving the oil floating on top. The oil is then taken from the water or the water (now containing the silica) is drained from beneath the oil. The silica may be removed from the water by, e.g., generally known methods of filtration and/or centrifugation followed by a drying step. The silica may be put to further use or may be treated to make it hydrophobic again. One method, e.g., is to treat the dry fine-particle silica with anhydrous gaseous HF, thereby making it hydrophobic such as in my co-filed application Ser. No. 730,541 filed Oct. 7, 1976 now U.S. Pat. No. 4,054,689. Also, the silica may be useful as is, e.g., as a filler or in compounding or rubber. The silica may be reacted with aqueous HF to form aq. H_2SiF_6 (see, e.g., U.S. Pat. No. 2,535,036) which may be employed as feed to a high temperature pyrolysis to form fumed, hydrophobic SiO_2 such as in U.S. Pat. Nos. 2,819,151 or 3,203,759. Such fumed, hydrophobic SiO_2 is particularly suitable for use as the fine-particle SiO_2 of the present invention.

Continuous operation may be performed by adding the hydrophobic silica to an oil-containing flowing body of water at a given addition point in the flow, then removing the oil-sorbed silica from the flow at a removal point downstream from the addition point, the interval of time between the addition and removal of the silica being less than that required for a change in the silica from hydrophobic to hydrophilic.

The following examples are embodiments illustrative of the practice of the invention but are not all-inclusive of all possible embodiments which will become apparent to practitioners of the invention.

EXAMPLE 1

Four grams of oil having a specific gravity of about 0.8 are spread on the surface of water contained in a 250 ml. beaker. When 0.4 grams of hydrophobic fumed silica containing sorbed HF values are poured on the surface and gently stirred, the fumed silica is not completely wet by the oil and appears to be in excess of what is required to form the oil into a flaky material; a lesser amount of the silica would be sufficient. The so-formed flaky material is easily removed from the water. The flaky oil-sorbed silica, when placed in water overnight releases the silica as the hydrophobicity of the silica is overcome and the silica goes into the water phase, leaving the oil floating on top of the water.

EXAMPLE 2

A gently flowing stream of waste water containing a layer of oil is treated with hydrophobic fine-particle silica in a generally continuous manner and the layer of oil-sorbed silica which forms is continuously skimmed from the surface of the water at a point immediately downstream from the point of addition. Very little of the oil remains in the water flow after the oil-removal step.

The oil-sorbed silica is left standing on water in a separation vessel for several hours, during which time the silica losses it hydrophobicity and enters the water phase, leaving the oil floating on top. The water phase is drained from beneath the oil, the silica is separated for further processing, and the water is cycled for further processing or is sent to the flowing stream of waste water, preferably at a point upstream from the silica-addition point.

The silica from Examples 1 and 2 above are rendered hydrophobic again by being treated with anhydrous, gaseous HF thereby obtaining silica having sorbed HF values. Such "regenerated" hydrophobic silica is reusable for adsorbing oil from water.

What is claimed is:

1. A method for separating oil from water comprising, in sequence, the steps of
   - adding to an oil-containing body of water an amount of finely-divided silica, said silica being characterized as containing sorbed HF valus which render the silica hydrophobic,
   - the amount of said silica being an amount sufficient to sorb at least a portion of the oil, thereby creating a bouyant layer on the water comprising oil sorbed on hydrophobic silica,
   - separating the said bouyant layer from the water,
   - adding the hydrophobic silica containing sorbed oil to a body of water,
   - allowing the hydrophobic silica to remain in contact with the water until the silica becomes hydrophilic by losing its hydrophobicity, thereby entering into the water phase and releasing the sorbed oil, thus forming an oil layer,
   - separating the resultant oil layer from the water, and
   - separating the silica from the water.

2. The method of claim 1 wherein the silica employed is hydrophobic, fumed silica.

3. A method for separating oil from water comprising, in sequence, the steps of
   - adding to an oil-containing body of water an amount of finely-divided silica, said silica being characterized as containing sorbed HF values which render the silica hydrophobic,
   - the amount of said silica being an amount sufficient to sorb at least a portion of the oil, thereby creating a bouyant layer on the water comprising oil sorbed on hydrophobic silica,
   - separating the said bouyant layer from the water,
   - adding the said bouyant layer to a body of water,
   - allowing the hydrophobic silica to remain in contact with the water until the silica becomes hydrophilic by losing its hydrophobicity, thereby entering into the water phase and releasing the sorbed oil, thus forming an oil layer,
   - separating the resultant oil layer from the water,
   - separating the silica from the water, and
   - rendering the silica re-cyclable by treating it with anhydrous, gaseous HF to renew its hydrophobicity.

4. The method of claim 3 wherein the silica employed is hydrophobic, fumed silica.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,151,078
DATED : April 24, 1979
INVENTOR(S) : Donald W. Calvin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 12; change "anhyrous" to --anhydrous--.

Column 1, line 21; change "Adside" to --Aside--.

Column 2, line 43; insert --with-- between "off" and "the".

Column 3, line 30; change "or" to --of--.

Column 4, line 8; change "losses" to --loses--.

Column 4, line 8; change "it" to --its--.

Column 4, line 25; change "valus" to --values--.

Signed and Sealed this

Eighteenth Day of *September 1979*

[SEAL]

Attest:

LUTRELLE F. PARKER

Attesting Officer *Acting Commissioner of Patents and Trademarks*

nited States Patent [19]

arrenchak et al.

[11] **Patent Number:** **5,037,557**

[45] **Date of Patent:** **Aug. 6, 1991**

1] **TREATED SILICA FOR OIL ABSORPTION**

5] Inventors: **James F. Warrenchak**, Albany; **Edward F. Phelan**, Troy, both of N.Y.

3] Assignee: **General Electric Company**, Waterford, N.Y.

1] Appl. No.: **569,251**

2] Filed: **Aug. 15, 1990**

Related U.S. Application Data

3] Continuation of Ser. No. 405,919, Sep. 12, 1989, abandoned.

1] **Int. Cl.**^{5} **C02F 1/28**

2] **U.S. Cl.** **210/691**; 210/924

8] **Field of Search** 210/671, 680, 691, 242.4, 210/924

6] **References Cited**

U.S. PATENT DOCUMENTS

2,819,151	1/1958	Flemmert	423/337
2,938,009	5/1960	Lucas	260/37
3,004,859	10/1961	Lightenwalner	106/308
3,053,627	9/1962	Flemmert	423/336
3,203,759	8/1965	Flemmert	423/337
3,382,170	5/1968	Pape	210/36
3,562,153	2/1971	Tully et al.	210/680
3,635,743	1/1972	Smith	106/490
3,847,848	11/1974	Beers	260/18
4,054,689	10/1977	Calvin	427/215
4,151,078	4/1979	Calvin	210/671
4,526,780	7/1985	Marschner et al.	424/66
4,536,399	8/1985	Flynn et al.	514/63

FOREIGN PATENT DOCUMENTS

84402719.3	7/1985	European Pat. Off. .

Primary Examiner—Ivars Cintins

Attorney, Agent, or Firm—Mark R. Warfield

[57] **ABSTRACT**

Fumed silica treated with octamethylcyclotetrasiloxane or hexamethyldisilazane are disclosed for the absorption of hydrocarbon spills, particularly on a body of water without the absorption of water.

6 Claims, No Drawings

TREATED SILICA FOR OIL ABSORPTION

This application is a continuation of application Ser. No. 405,919, filed Sept. 12, 1989, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a method using fumed silica as a hydrophobic sorbent material, particularly for the sorbing of hydrocarbons from the surface of water.

A serious problem which long has plagued industrial and environmental concerns is the removal of hydrocarbons, particularly oil, from unwanted areas into or onto which it has been discharged. Of particular concern is the removal of discharged oil from water or shore areas which occurs as a result, for example, of oil tanker accidents at sea or mishaps in the loading or unloading of oil from these tankers in port. Other occasions where hydrocarbon removal is of concern range from problems such as the discharge of oil at areas around oil wells and oil storage facilities or the cleaning of surfaces in which oil was stored (e.g. on-shore storage tanks, holds of tankers, etc.) to problems such as the discharge or leaking of oil from vehicles onto roads or driveway surfaces. Further, oil-water emulsions which are used, for example, as cutting fluids require separation of oil from the water prior to disposal.

Numerous solutions have been proposed for dealing with the problem of removing hydrocarbons from unwanted areas. One of these solutions involves the use of bacteria to degrade the hydrocarbons. However, such methods are expensive, raise important environmental concerns, and are often ineffective in cold weather environments.

Another solution to the problem lies in the use of absorbents which are intended to remove the hydrocarbons from unwanted areas by the use of physical forces rather than chemical break down of the hydrocarbons, i.e. where it is drawn into the absorbent material in much the same way water is drawn into a sponge.

Numerous examples of absorbents of this type are found in the literature. In U.S. Pat. No. 3,630,891 there is disclosed an oil absorbent prepared from wood fibers which have been treated with sizing material to render the fibers water repellant.

U.S. Pat. No. 3,770,575 discloses wet wood pulp treated with sizing and subjected to flash drying.

U.S. Pat. No. 3,382,170 discloses the use of perlite, a mineral containing silica, to absorb oil.

U.S. Pat. No. 3,591,524 discloses an oil absorbent comprised of cellulosic base impregnated with a complex oil-in-water, ammonium or amine-containing emulsion.

U.S. Pat. No. 3,756,948 discloses the use of polystyrene foam crumbs.

U.S. Pat. No. 4,131,543 discloses the use of insoluble silicate aggregates to absorb oil as well as other industrial solvents and acids.

U.S. Pat. No. 4,172,039 discloses the use of porous coconut husk material, such as coir dust, treated with an oleophilic-hydrophobic substance. The patent also discuss a method of absorption comprising the use of containers filled with the sorbent and which float on the surface of the water thereby absorbing the oil.

U.S. Pat. No. 4,343,680 discloses enhancing the oleophilic-hydrophobic properties of wood pulp by heating and fluffing.

U.S. Pat. No. 4,670,156 discloses the use of fibrous cellulosic material, e.g. sulphite reject, which is subjected to forced heating to enhance hydrophobic and oleophilic properties.

Some of the limitations of the examples mentioned above include prohibitive cost; ineffectiveness in extreme environmental conditions; tackiness of the material after it is saturated with oil; retention of oil in the absorbent until the absorbent is removed from the water; and ineffective or temporary hydrophobic characteristics.

In order to effectively remove hydrocarbons from water it is necessary that the absorbent absorb only the hydrocarbon and not the water. That is, the material should be both oleophilic and hydrophobic. Fine particulate silica has been known to exhibit both of these properties. See for example U.S. Pat. No. 4,054,689 which discloses silica treated with HF in order to make the silica hydrophobic without disturbing its oleophilic properties. The resultant material readily absorbs oil from the surface of water. However, upon standing in water for a number of hours, the silica loses its hydrophobicity, becomes hydrophilic, and enters the water, leaving the oil floating on top.

The aforementioned U.S. Pat. No. 3,382,170 discloses that the mineral "Perlite", which contains 65%-75% by weight SiO_2, exhibits hydrophobic properties upon treatment with an emulsion of polydimethylsiloxane in water at 200° C. to 500° C.

U.S. Pat. No. 4,526,780 discloses the use of fumed silica as a suspending agent in a deodorant composition which aids in the absorption of silicone oils. However, it is also taught that fumed silicone alone will not yield a stable product because the oil separates out.

U.S. Pat. No. 4,708,997 discloses the treatment of hydrophilic silicon dioxide with polydimethyldichlorosilane in order to render the material hydrophobic. This material is then used as one part of a suspending agent in the water-in-oil suspension polymerization of water soluble monomers.

U.S. Pat. No. 4,191,677 discloses the use of "TULLANOX" fumed silica to prevent water absorption in a two-part epoxy adhesive system.

U.S. Pat. No. 4,536,399 discloses the use of fumed silica to absorb oil from skin.

Although no documentation has been found for support, it is understood that Cabot Corporation has experimented with hexamethyldisilazane (HMDZ) treated fumed silica for absorption of crude oil on sea water.

The problem with using amorphous silica, and in particular fumed silica, is that it is normally hydrophilic and oleophilic. A treatment process is needed in order to render the material hydrophobic, and these treatment process are not always permanent. That is, after a period of time after exposure to water the silica often reverts back to its original hydrophilic property.

Another problem is that after treated silica is exposed to and has absorbed the hydrocarbons, the material does not agglomerate. Thus, is is difficult, if not impossible, to recover the saturated material without the use of very fine mesh screens.

It is therefore an object of this invention to provide a method for absorbing hydrocarbons from water while not absorbing the water.

It is further an object of this invention to provide a method for recovering hydrocarbons from the surface of water by the use of an absorbent material that can remain in water indefinitely without losing its hydrophobicity.

It is further an object of this invention to provide a method for recovering hydrocarbons from the surface of water by the use of an absorbent material that can be easily recovered after becoming saturated with the hydrocarbons.

It is further an object of this invention to provide a method for recovering hydrocarbons from the surface of water by the use of an absorbent material that is both hydrophobic and oleophilic.

Other objects will become apparent to those skilled in the art upon reading the following.

SUMMARY OF THE INVENTION

There is provided by this invention a method for absorbing hydrocarbons from water comprising the steps of:

(a) adding treated fumed silica onto the surface of water and hydrocarbon mixture; and

(b) gently agitating the water, hydrocarbons and fumed silica mixture.

DETAILED DESCRIPTION OF THE INVENTION

The fumed silica that is contemplated by this invention is that formed by the pyrogenic process as taught by Spialter et al. in U.S. Pat. No. 2,614,906 and Hugh et al. in U.S. Pat. No. 3,043,660, hereby incorporated by reference. For example, fumed silica filler may be made by burning silanes, e.g. silicon tetrachloride, trichlorosilane, etc. The resultant silica has a surface area of at least 50 m^2 per gram and preferably from about 100 to about 500 m^2 per gram. Most preferably the fumed silica will have a surface area of from about 150 to about 250 m^2 per gram.

The treating agent used to treat the fumed silica is any material which renders the fumed silica essentially hydrophobic without affecting its oleophilic properties. Preferably the filler is treated with a cyclic siloxane as taught by Lucas in U.S. Pat. No. 2,938,009 or by Brown in U.S. Pat. No. 3,334,062, hereby incorporated by reference.

Alternatively, the fumed silica may be treated with ammonia or a silazane as taught by Smith in U.S. Pat. 3,635,743 or by Beers in U.S. Pat. No. 3,847,848, hereby incorporated by reference.

The best treating agent as far as imparting superior hydrophobicity while maintaining oleophilicity is 2,4,6,8-octamethylcyclotetrasiloxane (tetramer). An alternative, although less preferred, fumed silica is one that is first treated by 2,4,6,8-octamethylcyclotetrasiloxane and subsequently treated by hexamethyldisilazane (HMDZ).

The fumed silica that has been treated by any of the processes described above will selectively absorb hydrocarbons while not absorbing any water. The hydrocarbons contemplated by this invention include industrial solvents such as toluene, benzene, methylethylketone (MEK), tetrahydrofuran (THF), mineral spirits, etc.; acids such as acrylic acid, etc.; high molecular weight alcohols; and monomers such as vinyl chloride, styrene, etc.

The treated fumed silica of this invention is particularly well suited for absorption of crude oil and products derived therefrom, including gasolines and diesel fuels, motor oils, heating oils, etc. The treated fumed silica of this invention is also well suited for absorption of oil from oil in water, [illegible] metal cutting processes.

In utilizing this invention in connection with an oil spill on the open seas or other bodies of water, the above described fumed silica is spread upon the oil layer, which floats on the water, by use of boats or airplanes. The fumed silica may be propelled in the nature of a jet stream into the oil layer from above which causes the same to penetrate the oil and to mix with it efficiently. Alternatively, the wave action of the water itself may be used to mix the oil and the fumed silica. In any event in order to maximize the effectiveness of the oil absorption, the fumed silica must be gently mixed into the oil phase. It would be most advantageous to introduce the treated, fumed silica at the water/oil interface, because this would decrease any handling problems caused by the low density silica.

Upon exposure of the treated fumed silica of this invention to oil the fumed silica becomes substantially saturated with about 1 to 10 times its own weight in oil. The fumed silica of this invention has a selective absorption whereby it shows a preference for the oil rather than for the water. Thus, even when previously soaked in water before spreading the same upon an oil spill, it will be found that this absorbent material is saturated with oil and rejects the water when spread upon a spill.

Upon becoming saturated with oil, the fumed silica of this invention transforms from a powder into globules that range in size from 1/16th inch to 2 inches or greater. Also, even after being saturated with oil, the fumed silica is less dense than water. Thus, the globules will float for periods of 30 days or longer upon the surface of the water allowing for easy recovery by skimming, screening, or filtering.

In order to maximize the amount of oil absorption by the fumed silica while still being able to easily separate the resulting globules from the water it is necessary to use an excess of silica. If less than an excess is used the resulting globules are tacky and are hard to screen off.

It has been found that 100 gallons of oil may be absorbed by from about 120 pounds to about 180 pounds of treated, fumed silica filler. More preferably, 100 gallons of oil may be absorbed by from about 150 to about 165 pounds of treated, fumed silica filler. It is recognized, however, that precise measurements of oil on the surface of a body of water may not be possible. In such a case the application of treated fumed silica to a depth of at least about 1 to 1.5 centimeters onto the surface of the oil will suffice. The actual amount necessary to absorb the oil is dependent on the viscosity of the oil and the thickness of the oil layer. The greater the viscosity of the oil, the more fumed silica is necessary for complete absorption.

Still another use of the fumed silica of this invention would be as a material to absorb hydrocarbons out of a mixture or emulsion of such with water. The discharge from the ship's bilges and from the flushing of tankers and barges could be handled in this manner so that the discharged water would be clean enough to cause no pollution problems and the silica material, after saturation with the oil, could be transported to a point of recovery or disposal. Another use for such a filter of this material might be in the absorption of oil that is emulsified with water, such as that used in the machine tool industry as a coolant during drilling and grinding operations, in order to purify the water and reduce pollution from its discharge.

Another use of this invention might be in the absorpon of oil that is spilled on land, for example a well head r around a storage tank, so that the oil could be safely ransported by any ordinary bulk container means to a oint of disposal. In this application, the fumed silica, as ereinabove described, would merely have to be emulified with water and mixed with the oil contaminated ground. As the fumed silica absorbs the oil, globules will form which can easily be collected and disposed of.

In some cases, oil spills reach sandy beaches to polute the same. To clear up such a beach, the oil contaminated sand may be mixed with an emulsion of the fumed ilica of this invention and water and then, upon contact with the sand, the oil would remain in the fumed silica and the clean sand recovered.

High or low ambient temperatures have no effect upon the absorption of oil according to this invention.

Only gentle agitation is necessary to cause the absorpion of hydrocarbons according to the teachings of this nvention. In fact gentle agitation is preferred since violent agitation may tend to cause the treated, fumed silica to act as a surfactant and form an oil-in-water emulsion. Preferred agitation is exemplified by a gentle wave action on a body of water which causes the water, oil, and silica to gently mix.

While this invention has been described chiefly in connection with crude oil, which has been involved in many spills on the high seas, it is also effective in absorbing gasoline, fuel oil, kerosene, emulsified oil, refined oil with additives, motor oil, cutting oil, and other hydrocarbon oils. The primary requirements for the hydrocarbon are the specific gravity, it must be less dense than the water so as to float. And, it should not be soluble, or only slightly soluble, in the water.

The following examples illustrate the oil absorption characteristics of treated fumed silica. The examples are intended to illustrate to those skilled in the art the process of this invention, and they are not intended to limit the scope of the invention in any way.

EXAMPLE 1

A 2.5 gallon container was ½ filled with water, creating approximately 270 cm^2 of water surface area. Into the container was then added either #6 Fuel Oil (FO), #634 Mobile Gear Oil (MGO), or a combination of equal parts of #6 FO and #634 MGO according to Table I. To the water/oil combination was then added treated fumed silica according to Table I.

TABLE I

	SAMPLE			
	A	B	C	D
Fumed silica (amount — gm)	11.0	18.0	8.2	8.2
Treating agent	OMCTS	OMCTS	OMCTS/ HMDZ	OMCTS
Surface area (m^2/gm)	200	200	200	325
Oil type	#634MGO	#6FO	#6FO	#6FO
Oil (amount — gm)	62.0	51.0	50.0	55.0

After bubbling compressed air into each container to agitate each sample the results were as follows:

Sample A: The silica absorbed 100% of the oil and formed globules ranging in size from ½ to 2 cm which were easily screened off.

Sample B: The silica absorbed 95.3% of the oil. The remaining oil sank to the bottom, preventing absorption by the silica. Slightly more mixing was needed than in Example A. Some silica flew off the top of the surface during bubbling.

Sample C: The silica absorbed 98.4% of the oils. Globules of 4 to 6 cm were easily screened from the clear water that remained.

Sample D: The silica did not completely absorb the oil and no free floating globules were formed.

What is claimed is:

1. A method for absorbing hydrocarbons from water consisting of the steps of:
   (a) adding a material consisting of treated fumed silica onto the surface of water and hydrocarbon mixture, the fumed silica having been treated so as to render it oleophilic and permanently hydrophobic; and
   (b) agitating the water, hydrocarbons and fumed silica mixture,

wherein the silica forms free flowing globules upon being saturated with the hydrocarbons.

2. The method of claim 1 wherein the silica has a surface area of at least 50 m^2 per gram.

3. The method of claim 1 wherein the silica has a surface area of from about 100 m^2 per gram to about 500 m^2 per gram.

4. The method of claim 1 wherein the silica has a surface area of from about 150 m^2 per gram to about 250 m^2 per gram.

5. The method of claim 1 wherein the silica is added so that there is a layer of from about 1 to about 1.5 cm of silica on the surface of the water and hydrocarbons.

6. The method of claim 1 wherein the water, hydrocarbons and fumed silica mixture is agitated by the wave action of the water.

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United States Patent [19]

Calvin

[11] **4,054,689**

[45] **Oct. 18, 1977**

[54] **METHOD OF PREPARING HYDROPHOBIC SILICA**

[75] Inventor: **Donald William Calvin**, Zachary, La.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

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[51] **Int. Cl.**^{2} **C01B 33/18; C09C 3/00**

[52] **U.S. Cl.** .... **427/215**; 106/288 B; 106/308 B; 423/267; 423/335; 427/255

[58] **Field of Search** .... 423/335, 267; 106/288 B, 308 B; 427/215, 255

[56] **References Cited**

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Primary Examiner—Jack Cooper
Attorney, Agent, or Firm—Walter J. Lee

[57] **ABSTRACT**

Amorphous silica is rendered hydrophobic by treating the silica with hydrogen fluoride vapors. The hydrophobic silica thus produced is useful in applications wherein either the sorbed fluoride values are desired or else the hydrophobic properties are desired. The hydrophobic properties are overcome by extended contact with water and the silica then becomes hydrophilic.

7 Claims, No Drawings

METHOD OF PREPARING HYDROPHOBIC SILICA

CROSS-REFERENCE TO RELATED APPLICATION

In my co-filed application Ser. No. 730,556 filed Oct. 7, 1976 titled "Removing Oil From Water," it is shown that a fine-particle hydrophobic silica, identified as a silica containing sorbed fluoride valves, is useful in sorbing oil from water. Such silica, containing sorbed oil, will become hydrophilic after standing for a time on water, thereby releasing from the oil and dropping into the water phase.

BACKGROUND OF THE INVENTION

Fine-particle size silica (SiO_2) is a commercialy available and useful product. Fumed, amorphous silica is known to be prepared, e.g., by pyrolyzing silicon halides in processes called vapor phase hydrolysis. When the silicon halide is a silicon chloride, e.g., $SiCl_4$, the fumed silica formed is hydrophilic. When the silicon halide is a silicon fluoride, e.g., SiF_4 or H_2SiF_6, the fumed silica formed is hydrophobic. Such hydrophobic silica will lose its hydrophobicity and become hydrophilic when in contact with water for extended periods of time.

Among the commercially available fine-particle silicas are those, e.g., bearing the tradenames Syliod, Cab-O-Sil, Zeosyl, Imsil, and Aerosil.

There is a need for methods of converting hydrophilic silica to hydrophobic silica, even silica which had previously been hydrophobic but which has become hydrophilic.

Patents which teach the preparation of fumed silica are, e.g., U.S. Pat. Nos. 3,053,627; 2,819,151; and 3,203,759.

U.S. Pat. No. 2,535, 036, e.g., teaches to react SiO_2 with HF to form fluorosilicic acid (H_2SiF_6).

U.S. Pat. No. 3,862,307 teaches to treat SiO_2 with aqueous HF to acidify the SiO_2 and provide fluoride values in dentifrice formulations. It is obvious that when aqueous HF is employed, the SiO_2 is prevented from becoming hydrophobic, since the silica is thoroughly wetted throughout the treating step.

It is an object of the present invention to convert hydrophilic silica to hydrophobic silica.

It is another object to return a previously hydrophobic silica to its hydrophobic state after it has lost its hydrophobicity by having been treated with water or with an agent which has neutralized its fluoride values.

Another object is to improve the oleophilic properties of silica by rendering the silica hydrophobic.

These and other objects, which will become apparent to practitioners of the relevant arts, are attained by the present invention.

SUMMARY OF THE INVENTION

Fine-particle silica is treated with HF vapors to render the silica hydrophobic. The treatment is essentially performed in the substantial absence of liquid water, even though water vapor may be present in the HF vapors used in the treatment.

DETAILED DESCRIPTION OF THE INVENTION

Fine-particle silica is treated with vapors of anhydrous HF or by vapors created by passing air or an inert gas through an aqueous solution of HF. vapors emitted from boiling aqueous HF may be employed. It is preferred to employ anhydrous HF, since water, if it is liquid or becomes condensed in the silica, tends to overcome, or retard the formation of, hydrophobic silica. However, water vapor in the HF vapor may be tolerated if one chooses to provide the HF vapor by passing a flow of air or other inert gas through an aqueous solution of HF so long as the water vapor is substantially prevented from condensing in the silica.

The contacting of the HF vapors with the fine particle silica may be done in any manner which provides efficient contact of the HF with the silica. Dropping the silica countercurrently to the HF flow is one way; tumbling the silica in a vessel containing HF vapors is another way. Conveniently, and preferably, the silica is treated in a fluidized bed technique wherein vaporous HF is passed upwardly through a column bed of silica in a manner, and at a rate, which fluidizes the bed, thereby obtaining mobility of the silica particles and assuring substantially complete contact of the HF with the silica.

The temperature at which the anhydrous HF treatment of the silica is done is conveniently, and preferably, an ambient temperature in the range of about 20° C to about 30° C. Higher temperatures may be employed, but for economical and energy-conservation purposes, ambient temperature is preferred. Temperatures below about 19° C should be avoided because of the tendency of anhydrous HF vapors to condense too readily in the silica; temperatures above about 500° C should be avoided because of a tendency to desorb the fluoride values from the silica about as fast as the sorption can occur.

When aqueous solutions of HF are employed, the temperature of the HF/water vapor which is purged out by the use of air or inert gas must be kept at above the dew point of the particular HF/water mixture so as to avoid having water in liquid form in the silica. It will be readily understood that an azeotrope exists at 38% HF and that HF solutions above that concentration will evidentually reach a concentration of 38% when enough HF has been removed. Also, if HF solutions of less than 38% are employed, the azeotropic cencentration will be reached when enough water has been removed. it is preferred that low HF concentrations be avoided, but they may be used if the temperature is held above the dew point at the treating step. A safe temperature at which one may operate, to avoid any condensed water in the silica, is at least about 112° C, the boiling point of the azeotrope.

Alternately, the aqueous HF may be flashed to the silica treating step without the use of a sparging gas. It is important here also to keep the temperature during the treating step at above the dew point of the particular HF/water mixture being used in order to avoid having water in condensed form in the silica.

Any fine-particle silica or powdery silica may be used in the present invention, and it is preferable to employ ultra-fine silica, such as fumed silica, in order that the greatest amount of surface area be exposed to the HF treatment. Other forms of fine-particle silica are suitable, e.g., dry silica gel, colloidal silica (dried and pulverized), and precipitated silica (dried).

The Kirk-Othmer Encyclopedia of Technology provides a good source of background information on silicas, including fine-particle amorphous silicas which are of particular interest for use in the present invention.

Even fumed silica which has been agglomerated to rease its apparent bulk density, but in which the glomeration step has only slightly reduced the effec- e surface area of the silica, is quite suitable for use in e present invention.

As mentioned hereinbefore, the silica may be one ich was formed initially as a hydrophilic silica or y be one which was formed initially as a hydropho- silica, but which has lost its hydrophobicity, thereby coming hydrophilic.

The hydrophobicity is easily determined by placing a mple of the silica on the surface of water. If the silica ets easily and drops down into the water, then its drophobicity is either negligible or nil. If it takes om several minutes to several hours to drop down into e water, then it is substantially hydrophobic.

As used throughout this disclosure, the expression orbed" is meant to include fluoride values which are tained either physically or chemically by the SiO_2, gardless of whether the fluoride values are adsorbed, sorbed, or chemisorbed. There is analytical evidence at at least some of the fluoride values are chemisorbed reacted onto the silica surface as indicated by the esence of Si-F bonds on the silica.

The amount of sorbed HF values in the silica may be much as about 2% by weight. One may determine hen maximum "loading" has been reached, or at least osely approached, by passing a gaseous stream con- ining HF through a fluidized bed of silica while test- g the effluent gases leaving the silica for fluoride val- s. When fluoride values are detected leaving the silica d, the treatment should be stopped so as to avoid asting the silica. Once the silica is essentially com- etely loaded, additional contact with excess HF may use formation and emission of SiF_4 and/or H_2SIF_6 (as ell as excess HF), depending on the temperature and esence of water. Such formation and emitting of SiF_4 d/or H_2SiF_6 would be counterproductive if one de- res hydrophobic silica as the end result.

Various analytical techniques may be employed to tect the presence of fluoride values in the gas stream aving the silica treatment step in order to determine if sentially complete loading has occured. A very con- nient method is to use an acid-sensitive "rag" or per which undergoes a color change when contacted ith acidic fluorine values.

Throughout this disclosure, the term "hydrophobic" eans that the silica is not readily wetted by water, but apparently oleophilic and readily absorbs oils such as iphatic hydrocarbons. One of the presently proposed es of hydrophobic silica is to sorb oil from the surface f water, thereby forming a flaky mixture of oil and lica which is readily separated from the water. The lica may then be separated from the oil by placing the ixture of oil and silica on water and allowing it to and for a number of hours, during which time the lica loses its hydrophobicity and enters the water, aving the oil floating on top. Silica which has lost its ydrophobicity and becomes waterwettable is consid- red herein to be hydrophilic.

The minimum extent to which the silica should be eated to acquire hydrophobic properties is determin- ble by placing the silica in water to see if it wets adily. Ordinarily, silica which has less than about 00–500 ppm fluorine values will wet fairly rapidly, us the degree of hydrophobicity at that level of load- g is very slight or nil. As the level of loading is in- reased, the degree of hydrophobicity is increased. At about 600–700 ppm fluorine loading the silica exhibits a markedly greater degree of hydrophobicity that the 400–500 ppm level and the invention can be seen to be operable over the range of about 600 ppm to about 2%. The preferred loading is in the range of about 0.5 to about 2.0%; the most preferred range to give a high degree of hydrophobicity is about 1.0 to 2.0% loading. It will be understood that the apparent hydrophobicity of the silica will be affected by the uniformity of the sorbed fluorine values throughout the silica. For best results the silica should be tumbled, stirred, fluidized or otherwise moved about when being contacted with the HF in order to approach or attain uniform contact throughout.

The following examples are illustrative of the practice of the invention, but the invention is not limited to the specific illustration given.

EXAMPLE 1

Fumed silica (hydrophilic) is placed in a vertical column. Air is bubbled through a relatively large supply of 52% solution of HF and upwardly through the silica, thereby fluidizing the fumed silica. The temperature is above that at which the entrained water vapor will substantially condense. Air flow is continued until an acid sensitive rag shows a color change at the bed exit indicating escape of unreacted acid fumes. The silica product is found to contain 2% fluoride by weight and is found to exhibit a hydrophobic nature. The hydrophobic silica is found to sorb oil from the surface of water, thereby forming a flaky-appearing material which floats on water.

EXAMPLE 2

In similar manner to Example 1, gaseous HF is passed upwardly through a bed of hydrophilic fumed silica at a rate sufficient to fluidize the bed. When the flow rate of HF leaving the bed is found to be about equal to the flow rate of HF being fed to the bed, the flow is terminated.

The silica is found to contain about 2% by wt. fluoride values and is found to be hydrophobic.

Other methods for contacting the silica with the HF vapor may be employed, such as dropping the silica through a contacting zone which contains HF vapor such as by passing gaseous HF through a tumbling bed of silica. Another way is to place the silica in a vessel, evacuate the air from the vessel, and backfill the reduced pressure with gaseous HF. Other methods will become apparent to practitioners of the present invention, having learned of it from this disclosure, but it is believed that the most efficient method is that of using a fluidized bed technique as described above.

I claim:

1. A method of causing fine-particle silica to be hydrophobic, said method comprising
   providing a supply of substantially dry, fine-particle silica which is not hydrophobic and a supply of gaseous anhydrous HF or a gaseous HF stream containing water vapor,
   contacting the silica, in the substantial absence of liquid water, with the gaseous anhydrous HF or gaseous HF stream containing water vapor at a temperature above the dew point of the HF and the water vapor, when water vapor is present
   continuing said contacting until the amount of fluorine values sorbed by the silica is in the range of about 0.06 to about 2% by weight.

discontinuing the supply of HF vapor being supplied to the silica, and

recovering the so-formed hydrophobic silica.

2. The method of claim 1 wherein the fine-particle silica is fumed silica.

3. The method of claim 1 wherein the gaseous HF supply is provided by being carried in an inert gaseous carrier.

4. The method of claim 3 wherein the inert gaseous carrier is air.

5. The method of claim 1 wherein said silica is contacted with the gaseous HF stream containing water vapor.

6. The method of claim 1 wherein the amount of fluorine values sorbed by the silica is in the range of about 0.5 to about 2.0% by weight.

7. The method of claim 1 wherein the temperature is within the range of about 20° to about 30° C when a gaseous anhydrous HF stream is used and within the range of about 112° to about 500° C when a gaseous HF stream containing water vapor is used.

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