**WSRC-TR-2001-00237, Revision 0**

# Illinois Institute of Technology Report:
# IITB52 Antifoamer for Alternative Salt Processes

**D. P. Lambert**

**Westinghouse Savannah River Company**
**Savannah River Site**
**Aiken, SC 29808**

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**APPROVALS**

5-7-01

D. P. Lambert, Immobilization Technology
Date

5-7-01

R. H. Spires, Manager, Process Development
Date

5/14/01

J. T. Carter, Manager, HLW Process Engineering
Date

5-8-01

**J. F. Walker, TFA System Lead**
**Date**

## EXECUTIVE SUMMARY

The attached report is a summary of the work performed by Dr. Darsh Wasan, Dr. Alex Nikolov, and their researchers at the Illinois Institute of Technology (IIT) during FY01. IIT developed the IITB52 antifoam for SRTC in FY00 to minimize the foam produced during precipitation, washing and concentration of cesium and potassium tetraphenyl borate precipitate. The IITB52 antifoam has been very successful during continuous processing (prototypical of plant operation). However, there were several key issues where SRTC needed the experience and knowledge of IIT to resolve. As a result a subcontract was set up with Dr. Wasan and Dr. Alex Nikolov during FY01.

This subcontract requested IIT to perform the basic research necessary to understand the foaming mechanism and explain the effectiveness of the IITB52 antifoam agent in the Small Tank Tetraphenylborate Process (STTP). The following are the primary tasks requested in the Statement of Work, which specified the tasks to be completed in this subcontract:

(1) develop a basic understanding of the degradation and batch variability of the antifoam identified in FY00 testing,

(2) develop a basic understanding of the poor performance of the antifoam in washed precipitate as identified in FY01 testing,

(3) continue to supply the antifoam necessary for SRTC and ORNL testing, and

(4) provide insight into the fundamental science involved in the effective performance of the IITB52 antifoam agent.

The report did an excellent job of providing an explanation of the antifoaming mechanism. In addition, IIT supplied all the antifoam necessary for FY01 testing. However, there were two tasks that were incompletely covered in the report that was issued. The first is the basic understanding of the antifoam batch variability and the second is the basic understanding of the poor performance in washed precipitate. These two items will be addressed in a future revision of this report.

The first task will require collaboration between IIT and the antifoam manufacturers, Witco and Cytec. Are there any differences in performance due to manufacturing processing, solvent differences or shelf life issues that made Batch 2 antifoam less effective in foam column testing? Please provide insight into the probable reason for lower efficiency. If the solvent is responsible for the differences, a ternary diagram of the salt solution/water/IITB52 would show regions of solubility necessary for dilution and processing.

The second task is to develop a basic understanding of the poor performance of the antifoam in washed precipitate as identified in FY01 foam column testing. At antifoam concentrations as high as 3,000 ppm, the precipitate foamed up out of the column within 3 minutes. Samples of unwashed and washed precipitate should be compared in both foam column tests as well as in more prototypical process conditions.

# Report

# On IIT B52 Antifoamer for Alternative Salt Processes (New TPB Process)

by

**Alex Nikolov and Darsh Wasan**
**Department of Chemical and Environmental Engineering**
**Illinois Institute of Technology, Chicago IL 60616**

**Date: March 27, 2001**

## B52 Antifoamer for Alternative Salt Processing
## (New TPB Process)

## 1. **Introduction**

The Savannah River Site is developing an alternative salt process for the immobilization of high level nuclear waste materials such as cesium. One of the proposed high-level waste decontamination processes uses sodium tetraphenyl borate (NaTPB) to remove radioactive cesium from the caustic waste solution. The micron-sized precipitate, primarily potassium tetraphenyl borate (KTPB) and cesium tetraphenyl borate (CsTPB), is concentrated by crossflow filtration (as shown in Figure 1), washed, and hydrolysed, processed in the Defense Waste Processing Facility where it is vitrified for final storage as a stable glass form. In a recent precipitation/filtration experiments at SRTC, 60% excess NaTPB was used to assure effective cesium decontamination, 40,000X. During the slow addition/agitation/reaction/filtration process cycles some of the excess NaTPB decomposed to benzene and other mineral borates.

The immobilization process includes the formation of KTPB slurry. The process flow diagram of TPB precipitation is shown in (Figure 1). In reactors # 1 and #2 (Figure 1), the TPB precipitation takes place. The precipitation starts in reactor #1 where the input components NaTPB, MST, and waste are mixed. During mixing, air bubbles are incorporated into the slurry and foaminess is observed. The precipitation processes continue in reactor #2. The slurry is transferred to a concentration tank where the slurry concentration is increased to 10 wt% insoluble solids. The aqueous solution of the slurry contains 5 mol/liter electrolyte and the pH is highly alkaline. The foam is very high (several hundred volume percent) and the foam is very stable. A new antifoamer IIT B52 was developed (Subcontract # AE-14869S), and tested in laboratory scale experiments with simulated and actual waste at SRTC. The result for laboratory scale anti-foaming performance of IIT B52 is presented in report WSRC-TR-2000-00261.

The goal of this study is to provide a physical understanding of how IITB52 works.

## 2. IIT B52 Antifoaming Mechanism

The foaming mechanisms in the presence of KTPB particles were discussed in the report: subcontract # AE-14869S. During aeration, the KTPB particles are attached to the air/liquid surface of the floating bubbles and form a *particle structural stabilization barrier (PSSB),* thereby lending stability to the foam lamella. Figure 2 depicts the KTPB particle foam lamella stabilization mechanism.

The KTPB particles at high pH slowly decompose to benzene and the benzene is retained on the KTPB particles. With time, the KTPB particles aggregate and form a network structure (slurry). Benzene helps KTPB particles to aggregate and thereby stabilize the foam lamella. More information on the benzene retention process in ITP slurry is available in the final report of subcontract # AB94258S (2).

To eliminate foaminess, the particle foam lamella stabilization barrier must be broken. There are two ways of doing this: one way is to modify the biphilic (partially wetted) surfaces of the KTPB particles by removing the benzene from particle surfaces so that they become hydrophilic (water wetted), and cannot form a PSSB; and the second method is to break the PSSB by generating a surface tension gradient (local instability) at the air/slurry surface. These two methods can be combined to develop an efficient antifoamer.

IIT B52 is a polar molecule, and has hydrophilic and hydrophobic parts. The molecular polarity (biphilicity) from an engineering point of view, is characterized by HLB (hydrophile-lipophile balance). For example, HLB =1 means that the molecule is soluble in the oil phase. At HLB =40, the component is soluble in the water phase, and is insoluble in oil. A sketch of the molecular structure of IIT B52 is shown in Figure 3. The HLB of IIT B52 is about 20, and this means that the molecules of IIT B52 are soluble in water, and due to the attraction between the molecules, micelles or aggregates are formed. Because of its biphilicity, such a molecule has surface activity and can adsorb at the surface or interface (e.g. at aqueous solution/KTPB, and at air/aqueous surface). When IIT B52 is added to the KTPB slurry, molecules adsorb on the KTPB particles, remove benzene from the particle surface, and modify the surface to make it water wet, so that particles cannot form a PSSB (Figure 4). Moreover, the micelles solubilize (capsulate) the benzene removed from the particle surface, so the benzene removal is irreversible. Benzene cannot spread back onto particle surface.

During the agitation process, when the micelles (aggregates) reach the air/aqueous surface of the bubble covered with KTPB particles, a surface concentration gradient is created locally, which breaks the PSSB due to the local instability at the air/slurry surface. Figure 5 depicts the mechanism, which leads to destabilization of the PSSB caused by the surface tension gradient.

In summary, the newly developed IIT B52 antifoamer removes benzene from the KTPB particle surface, modifies the surface of the KTPB particles to make it more water wet. B52 washes and solubilizes benzene from the surface of the KTPB particle. Proof that IIT B52 is a good wetting agent and solubilizes benzene is the observation that the KTPB particles settle under gravity to the bottom of the vessel and are well dispersed (disintegrated). The aggregates formed by the molecules of B52 generate surface tension gradient. The surface tension gradient and its effect on PSSB destabilization can be demonstrated by placing a small waxy particle from pure B52 at the air/aqueous slurry surface. Some of the slurry particles due to biphilicity are attached to the air/aqueous surface and form a 2D-network structure. When the waxy particle of B52 is placed at the air/aqueous surface, due to the generated surface tension gradient, it dances at the air/water and breaks the PSSB. As a result of the KTPB particle surface modification and the generated surface tension gradient, the PSSB is destabilized and the foaminess is reduced.

## 3. Antifoam Formulation

The antifoaming performance of IIT B52 depends on its degree of water solubility and the formation of micelles (aggregates). The solubility is related to the solvent (water) and the solute (IIT B52) interactions. The primary material of IIT B52 is a waxy solid, and has a limited solubility in water (about 0.1 wt%). For instance, to dissolve 0.2 wt% (2000 ppm) of the material in water, it needs about 30 min to reach the equilibrium state. The solution contains micelles and aggregates (it is turbid). Therefore, the right organic solvent is needed, which will mediate the dissolution of the antifoamer into the aqueous medium. This requires that IIT B52 be dissolved in a primary friendly organic solvent, which dissolves it completely. It can then be stored for a long time without its molecular structure being affected. Moreover, when the primary IIT B52 solution is added and mixed into the aqueous phase of KTPB slurry, a solution with the right molecular and aggregate composition needs to be prepared, in order for the IIT B52 aqueous solution to have the best antifoaming performance. This is a tricky task.

A company such as AirProducts improves the antifoaming performance of its products (e.g., based on acetylenic diol) by selecting the organic solvent which creates a better environment (such as solubility and size of oil the droplet) when the antifoaming product is dissolved into the aqueous medium. From a thermodynamic point of view, the solvent/solute interactions have an impact on the degree of freedom, molecular structure, and conformation of the dissolved molecules (i.e., on the chemical potential). In a good solvent, the solute molecules are completely dissolved; in a poor solvent, the dissolved molecules form a dispersed phase or the phases separate. The Flory-Huggins theory for molecular solution introduces a solvent quality parameter, $\chi$, which characterizes the solvent solute interactions, e.g., for a good solvent $\chi$ is > ½ and for a poor solvent $\chi$ is < ½ [Ref. 1].

In summary, selecting the right solvent is important for good performance of the antifoamer. IIT B52 antifoamer was tested using two different primary solvents: ethanol and propylene glycol. The table below summarizes the composition and some physicochemical parameters and technical information (such as flammability) for the antifoamers tested by both SRS and Oak Ridge National Lab.

Ethanol (5-7 v%) is a good primary solvent for B52. However, when B52 ethanol (5-7 v%) solution is dissolved into the aqueous phase, the viscosity of the solution (1,000 ppm) is too high. Increasing the ethanol concentration to 10 v% helps to reduce the viscosity, but this increases the flammability of the solution. Propylene glycol, PG (5-7 v%) was also used as a primary solvent to dissolve B52. In this case the viscosity of the 10,000 ppm aqueous solution was low. The flash point of the B52-PG is higher than that of B52-ethanol solution (e.g., for 5 v% ethanol solution the flash point is ~100ºF, whereas for 5 v% PG solution flash point is ~200ºF. However, the antifoaming performance of B52 was less (see Table below). From a practical point of view the choice of solvent for B52is very important. Therefore, a short term study is recommended to select the best solvent for B52. This should include both propylene and ethylene glycols with different molecular weights and structures. The viscosity and turbidity (solubility) of the B52 solution should be measured, as well as the antifoamer performance.

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[1] R. Vold and M. Vold, Colloid and Interface Chemistry, p. 745, 1983, Addison Wesley Publishing Co., Advanced Book Program, UK.

## 4. B52 Antifoamer Characteristics

| Anti Foamer Lot | Vendor | Form | Activity | Solvent | Viscosity Centipoise (at 25ºC | Density $\rho_{H2O}$ =1 | Solubility in water (25ºC) | Flash Point | Antifoam Performance |
|---|---|---|---|---|---|---|---|---|---|
| Batch 1 | Witco | Solution | 75 % | Ethanol | >100 | 1.05 | ~ 4 wt% | ~100ºF | 100% |
| Batch 2 | Cytec | Solid | 70 % | Propylene Glycol | >300 | 1.1 | ~ 2 wt% | ~200ºF | ~25% |
| Batch 3 | Witco | Solution | 70 % | Ethanol | >100 | 1.05 | ~ 4 wt% | ~100ºF | 100% |

## 5. B52 Antifoamer Performance

The antifoaming performance of the three batches prepared at IIT was tested at SRS and the Oak Ridge National Lab. The antifoaming performance of Batch 2 was also tested at IIT, but in a different way than at SRS and ORNL. The antifoaming performance of B52 at IIT was tested in two ways: mixing (the antifoamer was added to the slurry before foam generation), and by adding the antifoamer over the foam surface (i.e. on the top) during the foam generation. In both ways, the antifoamers from Batches 1 and 3 showed excellent and higher performance than the antifoamer from Batch 2. In order to understand why the antifoamer from Batch 2 showed a lower performance during IIT testing than the antifoamers from Batches 1 and 3, one needs to analyze the experimental procedures. The foam testing at IIT was conducted by a foam column test, aeration of 10 wt% KTPB slurry by passing air through a sintered glass filter (for more information see the final report for subcontract # AE –14869S). The antifoaming performance was evaluated based on the reduction in foaminess shortly after it was added to the slurry.

The antifoaming performance of IIT B52 tested at SRS and ORNL was conducted in a different manner. The antifoamer was added during the slurry particle precipitation following the process flow diagram of TPB precipitation shown in Figure 5. In this procedure, the antifoamer molecules are adsorbed on the surface of the KTPB particles right after the nucleation step, and the particle surface is wetted from the time the particles were generated. The antifoam performance test results conducted at IIT, SRTC and ORNL do not correlate, because the testing procedures are not the same. For the correct evaluation of the antifoaming performance of the

B52, after the order and method of antifoam addition is crucial. All these important issues need further investigation.

## 6. Stability of B52 in a Caustic Medium

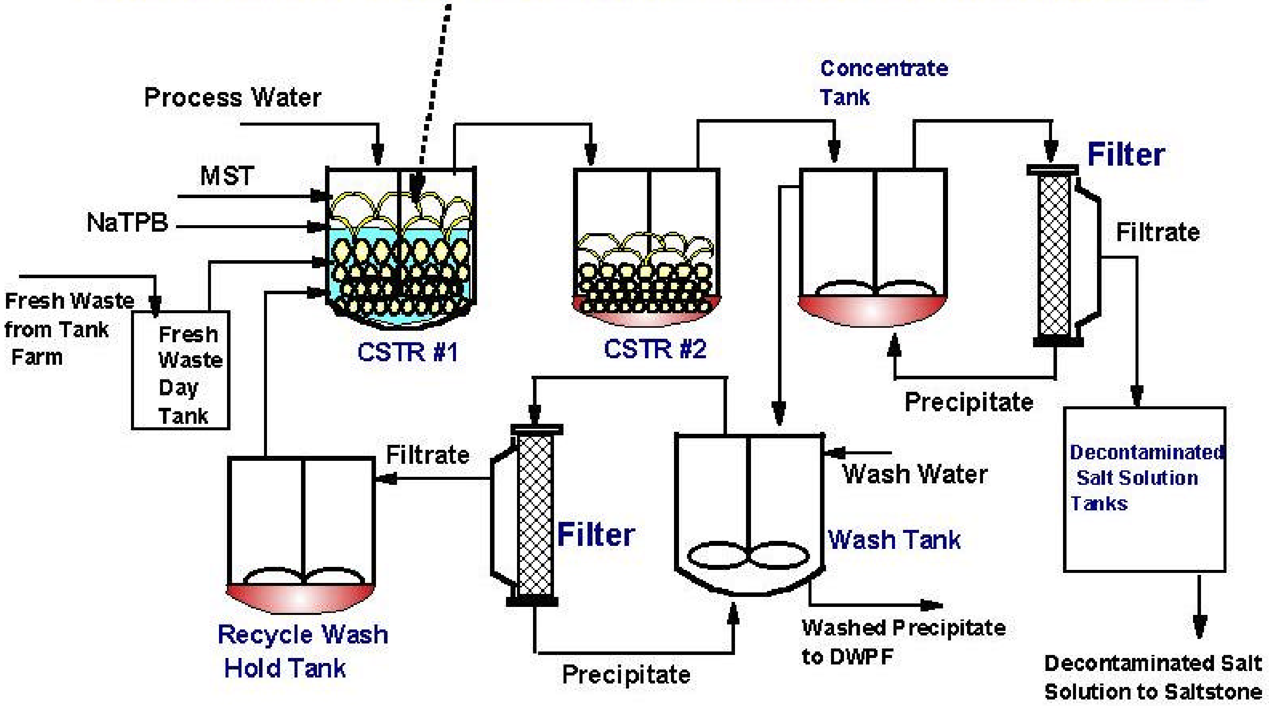
An important issue is the stability of IIT B52 when it comes in contact with the highly alkaline slurry. The antifoaming performance of IIT B52 was tested after a 24-hour pre-equilibration with KTPB slurry. The antifoaming performance of IIT B52 (tested by the foam column method at IIT), using an initial concentration of 1500 ppm decreases by 15 to 20 %. (see the final report of the subcontract # AE –14869S). However, an additional dose of only 100 ppm fresh B52 antifoamer was needed to completely eliminate the foaminess. This result shows that in the highly alkaline environment of KTPB slurry, B52 begins to decompose. The mechanism of hydrolysis of B52 in a highly caustic environment was discussed during the December 14, 2000 technical meeting held at IIT, and is shown in Figure 6. In a highly alkaline solution, the ester part of B52 decomposes to different types of Na-soaps. Some of these Na-soaps will act as good wetting agents. The by-products of hydrolysis will not promote foaminess and are non-toxic.

## 7. Manufacturing and Purchasing of Antifoamer

B52 antifoamer can be manufactured in the facilities of DeBourg Corporation under the supervision of the inventors: Dr. Alex Nikolov and Dr. Darsh Wasan of IIT. For more information about this option, a meeting with SRS representatives, the inventors of B52 and DeBourg Corp. is highly recommended. During this meeting the antifoamer test procedure needs to be discussed. Such a test has been discussed, and proposed in the past, however this test needs to be delineated, since the SRS and ORNL are adding the B52 to the KTPB slurry during the precipitation step of the process.

# Appendix

1. Subcontract #AE14869S – Alternative Salt Processing (New TPB Process), Final Report, July 4, 2000.
2. Report on Subcontract #AB94285S – Benzene Retention in ITP Slurry, February 10, 1997.



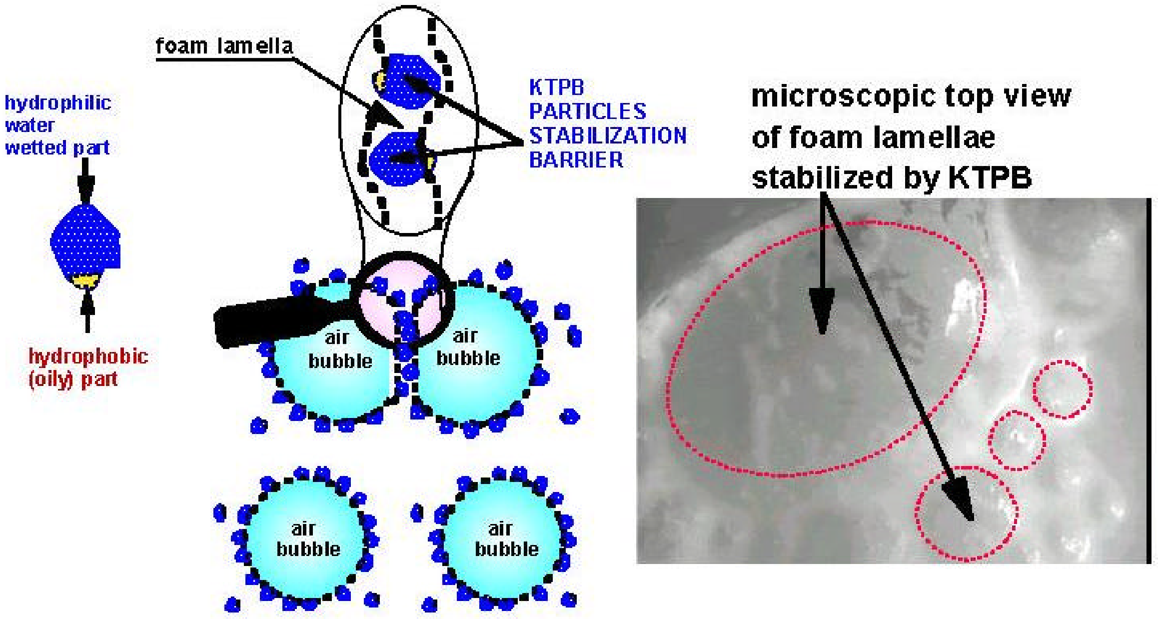
Foam is formed due to gas bubbles dispersed into the KTBP slurry

**Figure1**

**Process Flow Diagram of TPB Precipitation**

**High Level Waste Salt Processing**

# What Stabilizes the foam lamella?



FOAMINESS AND FOAM STABILITY IN THE PRESENCE OF KTPB PARTICLES IS DUE TO THE BIPHILIC NATURE OF THE PARTICLES. THE PARTICLE BIPHILICITY CAUSES THE FORMATION OF STRUCTURAL STABILIZATION BARRIER AT AIR/BUBBLE SURFACE.

FIGURE 2

# IIT B 52

## STRUCTURE-PERFORMANCE RELATIONSHIP

**HYDROPHOBIC LYOPHILIC**
**BALANCE**
**(HLB)**

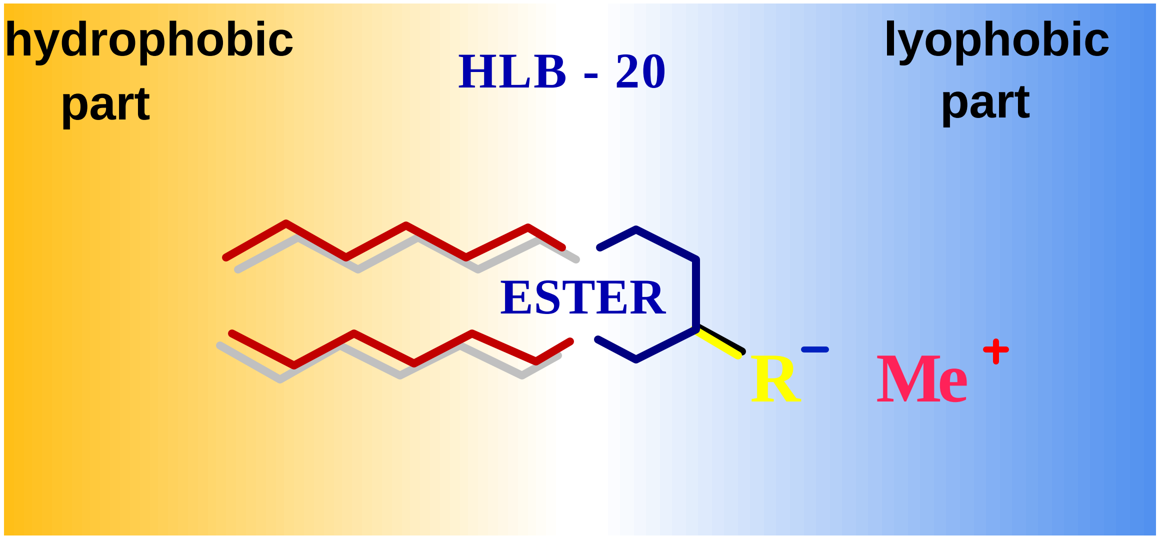


FIGURE 3

# How the B 52 antifoamer works ?

## PARTICLES STABILIZATION BARRIER CAN BE ELIMINATED BY CHANGING PARTICLE WETTABILITY (HLB)

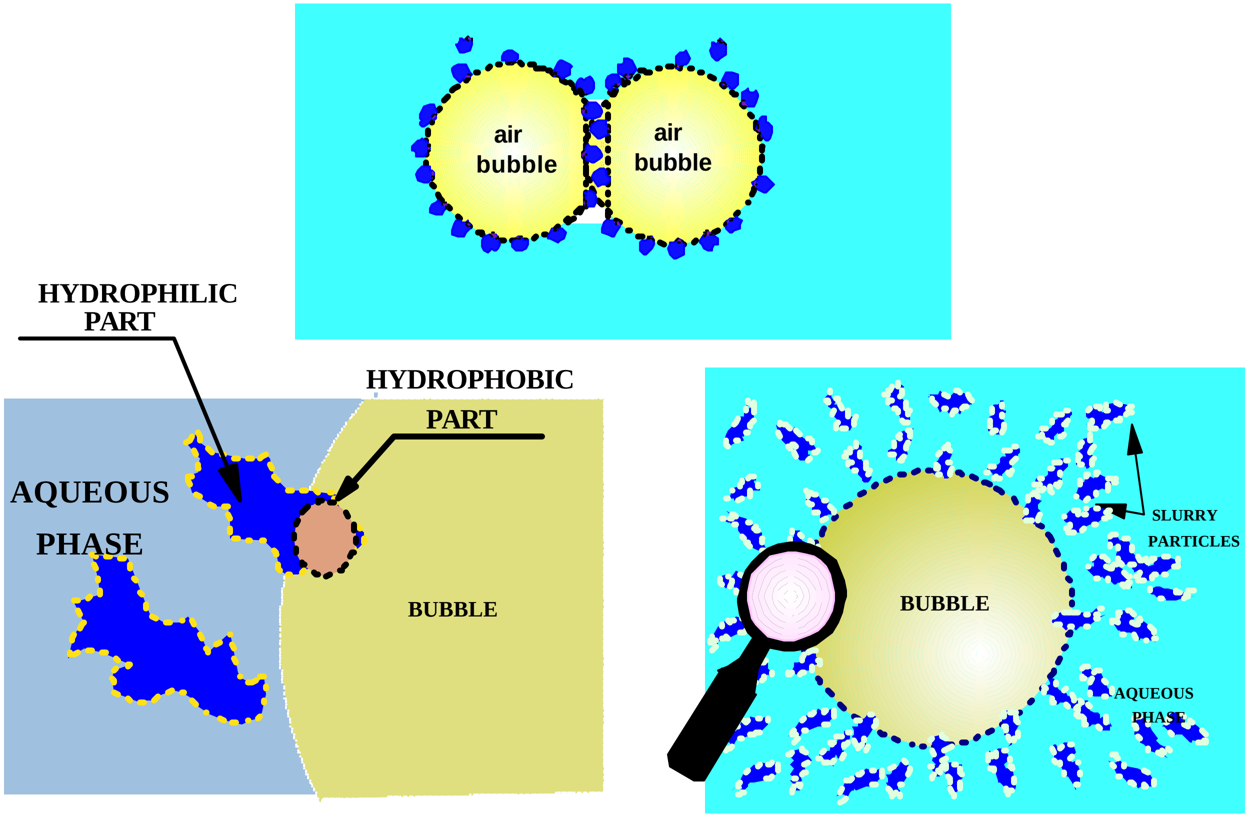
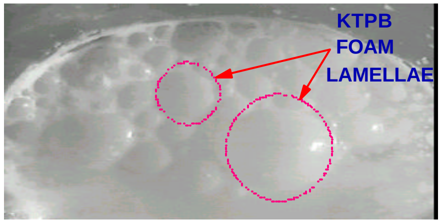
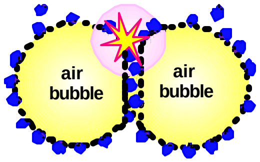


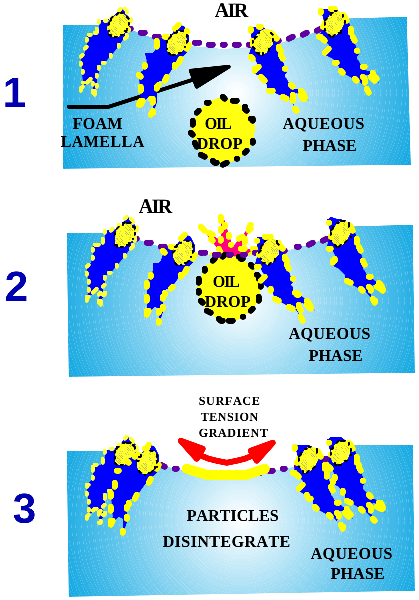
Figure 4

# HOW TO DE-STABILIZED THE PARTICLES BARRIER ?





BY STRETCHING THE SURFCAE OF THE FOAM LAMELLA THE PARTICLES STABILIZATION BARRIER DISINTEGRATES



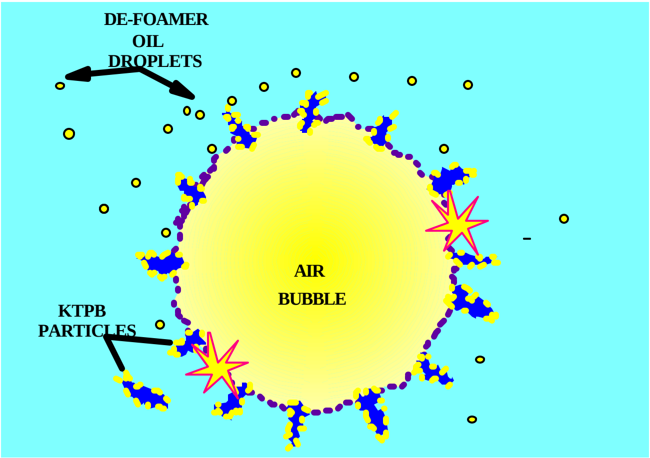


Figure 5

# IIT B 52

## EFFECT OF pH ON CHEMICAL STABILITY

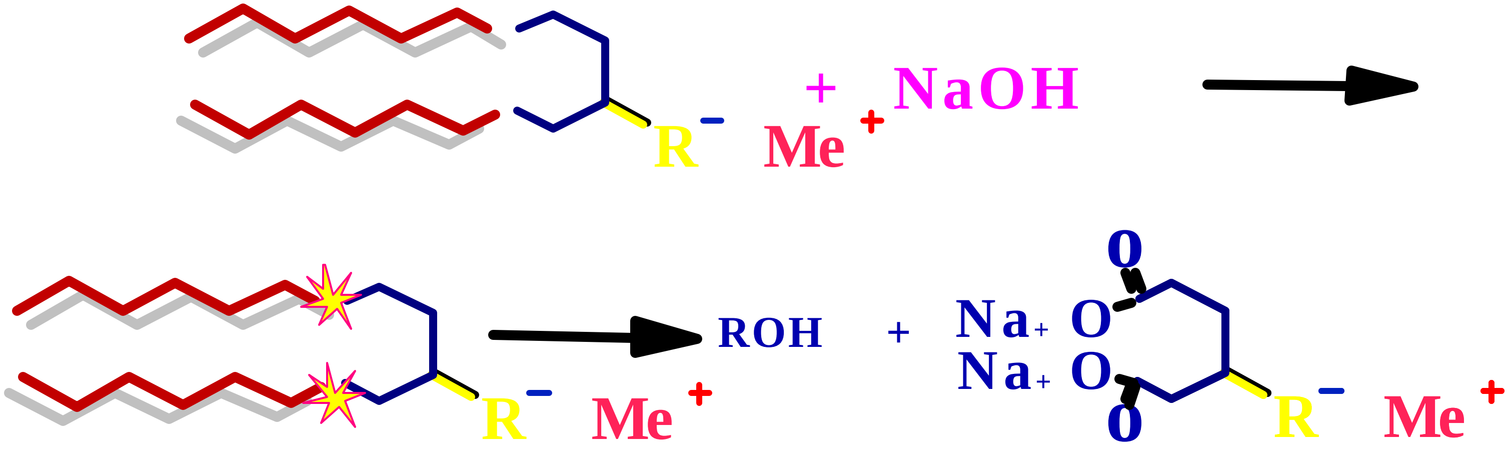


Figure 6

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