866 Horan Drive
Fenton, MO 63026
(800) 729-8220 toll-free
(636) 349-5333
claytoncorp.com

Review of the Phenomenon of Film Formation in cans of One Component Polyurethane Foam

By: Ric Berger & Jay Zhang

Before getting into the current problem of film formation (also known as skinning) it is important to understand possible causes of film formation along with some history of the problem. The possible causes for film formation which may allow this phenomenon to occur are:

1. Moisture in the can.
2. Improper mixing.
3. Metal Contamination.
4. Improper ingredient selection.

It is also important to understand a little bit about the chemistry of polyurethane one component foam (OCF) in order to understand how each of the causes listed above plays a part in the formation of a film on the surface of the liquid in the can.

Let's begin by looking at a list of basic ingredients in an OCF formulation:

1. Polymeric MDI (PMDI)
2. Polyols
3. Surfactant
4. Catalyst
5. Plasticizers
6. Blowing Agent

Note: For the purpose of this report we will call PMDI the A side, a blend of ingredients 2 through 5 the Polyol blend or B side and the blowing agent the propellant (In some areas of the world the meaning of the A side and B side may be reversed).

Some information on OCF polyurethane chemistry is useful to understand how a film forms. During the common OCF manufacturing process, PMDI reacts with Polyols to form isocyanate NCO terminated polyurethane prepolymer molecules. The ratio of PMDI to Polyol, A/B, is a very important factor and it directly affects the molecular size (molecular weight) of the resulting prepolymer. Here we can use a simplified mathematic equation to illustrate the effect of the A/B ratio on prepolymer molecular weight, MW.

$$M_W = m / (A/B - 1)$$

Where m refers to the molecular weight of the "mer", that is the repeating unit of the prepolymer.

A/B values for common OCF formulation are much higher than 1. The higher the A/B ratio, the lower the resulting prepolymer molecular weight. As results the final OCF material in the can will have lower viscosity. Reversely, when the ratio PMDI to Polyol is reduced, the lower A/B value leads to a higher prepolymer MW and a lower free NCO content. At the same time the OCF product becomes more viscous if the rest of formula remains unchanged. As an extreme case, when A/B ratio approaches 1/1 (stoichiometric system), the prepolymer molecular size becomes so big or even close to "infinite" that it can become a solid polymer.

Obviously, in the lower free NCO content OCF products, the prepolymer macules may be so big (so long) that it can be solidified with lesser amounts of water and it also becomes more sensitive to other factors, such as heavy metal or temperature, which reduce its shelf-life.

As a final understanding about this part of the chemistry I list the following OCF facts that will help us later:

1. If the ratio A/B equals one then the molecular weight of the molecule is infinite and the resulting mixture can become a solid.

2. The longer the molecule the more viscous the liquid.

3. The longer the molecule the less water that is needed to solidify the prepolymer.

We also need to understand the importance of mixing the ingredients to the formation of a proper prepolymer inside the can. There are two important factors to proper mixing, mixing efficiency and time until the can is mixed after filling. To understand the importance of proper mixing we will start by looking at the filling process of OCF can products. Can filling is done in the following steps:

Step 1. Inject the A side into the can.

Step 2. Inject the B side into the can.

Step 3. Place and crimp the valve on the can.

Step 4. Inject the propellant into the can.

Step 5. Shake the can.

Note: Additional steps may be included such as putting the can through a water bath, labeling, capping, attaching actuator and tube and packaging.

The effect of time until mixing: After injecting the A & B sides, one material is sitting on top of the other. At the interface where the two sides touch each other there is a 1 to 1 ratio of A to B. If the time between injecting the A and B materials is long enough (such as during break time), at the interface of the two materials, long molecules will form. By the end of the production process, these long molecules would be on the surface of the liquid and because of the lower amounts of water required for them to harden may harden to form a film.

Time plays a further factor even after injecting the propellant. While the process of injecting the propellant will result in some mixing of the two sides, it will not provide for adequate and uniform mixing. This will result in areas in the liquid where the ratio of A to B is close to 1 to 1. As described above these areas will result in long chain molecules which may end up forming a film on the surface of the liquid

Effect of inefficient mixing: Even though the can may be shaken to mix the A and B sides, if it doesn't fully blend the two materials forming a homogeneous mixture, there will be areas in the liquid where the ratio of A to B is close to 1 to 1. These areas will form long molecules and the result will be as described above.

The formation of a film on top of the liquid content is not a new phenomenon. One of the early causes of film formation was the result of improper mixing of the ingredients. This problem goes back to the start of one component polyurethane foam production. The problem appeared to have been eliminated in the 1990s as fillers learned of the importance to match product viscosity with shaking style and speed.

It was also learned in the 1980s the importance of using the right catalyst in order to prevent the product from hardening in the can. The original catalyst used would cause the product to start hardening in the can in a short period of time. This resulted in products with a short shelf life. With the introduction of DMDEE as a catalyst the shelf life was greatly extended. In the 1990s, I had cans that had been sitting in my office for five years. The cans used DMDEE as the catalyst and had a propellant blend of hydrocarbon and DME. When tested, these cans still worked and delivered good foam.

It was also known that moisture could be introduced into the system through the water content in raw materials such as Polyols and plasticizers. Moisture in the raw materials, depending upon the level, can result in an over pressurized can which may deform or explode in the worst case or hardening of the product if in very low levels. This is why incoming inspection of raw materials for moisture is important.

As fillers became aware of the issues mentioned above, the formation of a film on the surface of the product inside the can appeared to have been eliminated. It has just been over the last few years that we have seen film formation in the can return as a problem. It was first noticed in cans of a new gun foam product called Mega Foam (Mega foam is a product designed to provide a larger volume of cured foam than standard formulas). An investigation into the reasons why Mega Foam is developing a film has yielded the following information:

1. To increase the foam's volume (increase yield) more propellant was added to the product formulation increasing the propellant's percentage of the total formulation.

2. As a result of higher percentages of propellant, a larger/coarse cell structure was seen in the cured foam. Too improve the cell structure; a common approach used is to increase the chemicals solubility by adding a higher level of DME to the propellant blend.

3. The higher DME level results in a thinner product which dispenses too fast. To reduce the dispensing rate, the ratio of PMDI to Polyol is moved closer to 1 to 1 which results in a more viscous product and hence reduces the dispensing rate.

4. As a result of reducing the A/B ratio a longer and more moisture sensitive prepolymer molecule is formed.

How do the above changes in formulation technology and other formulation and material changes effect the formation of a film? Now that we have some background information on film formation, let's individually examine the four causes of film formation presented at the beginning of this report.

Moisture in the Can

Knowing the fact that moisture will cause the prepolymer to harden, let's begin our examination of film formation by looking at how moisture can get inside the can. Moisture can find its way into the can through a number of different paths including:

1. Condensation on the inside of the can before filling.

2. Empty cans exposed to rain or other water sources such as a leaking roof.

3. Water in the Polyol blend.
4. Water in the propellant.

5. Permeation of moisture through the valve.

6. Permeation of moisture through the can seams.

As is outlined in the list above, there are many potential sources from which water can gain entrance into the can. Let's examine each moisture source and review possible ways to eliminate the potential of a moisture source being the cause of film formation:

1. Condensation – Cans going from a warm/humid condition into a colder condition can cause condensation to form in the can. Cans stored under warm humid conditions either outside or in a warehouse and then brought into a colder filling area can cause moisture in the air to condensate on the can wall. Therefore, it is critical to control the storage conditions and conditions in the filling room to prevent the possibility of condensation forming.

2. Exposure to water sources – Water may enter the can as a result of such problems as a leaking roof or water pipe or from condensation dripping off of overhead pipes. It is important to store cans where there isn't a possibility of water getting into them. If there is a chance that water has gotten inside, make sure to dry the cans before use.

3. Water in the Polyol Blend – The water content of all raw materials should be controlled. All raw materials must be PU grade. That means they are produced to specific moisture content specifications. In USA the typical moisture content specification is less than 0.05%. In other parts of the world the typical moisture content specification may be up to 0.1%. The lower the better. It is important to obtain certifications from your suppliers as to the amount of water in each delivery. It is also import to test the materials for water as received. In some formulations you may need to reduce the amount of water allowed in the raw materials to help prevent the formation of a film, prevent cans from deforming or exploding during production and to maintain the shelf life requirement.

4. Water in the Propellant – This is a potential source of water contamination that has been overlooked until recently. Recently, a PU foam filler informed me that they found water in their propellant as received from their supplier. As with other raw materials, make sure your supplier knows the water content specification and you receive a certification with each shipment.

5. Permeation of Moisture through the Valve – Rubber has a low rate of moisture permeation as a characteristic of the material. Just as over time the propellant will permeate out of the can through the rubber, moisture will find its way into the can through the valve's rubber seal. Polyurethane prepolymer attracts moisture so it acts like a desiccate inside the can helping pull moisture through the valve's rubber seal into the can. This is not a leak of the valve in the sense of the valve being defective but a property of the rubber. The type of rubber used for the valve's seal has not changed so looking at the historical results of the valve you will see that this is not the reason for film formation in and of itself. It is possible

that changes in the formulas, used for such foams as Mega Foam, are affecting the valve's material differently which in turn may allow more moisture to permeate through the valve. Clayton is currently undertaking a study to determine if changes in propellant blends and fill volumes affect the moisture permeation rate of the rubber in the valve.

6. Moisture Permeation through the Can Seams and Crimp – Moisture is also capable of permeating through the seams of the can both on the can's side and at the connection of the top and bottom domes. Moisture will also permeate through the valve crimp. Clayton has found hardened polyurethane at these locations inside the can upon opening the can after long term storage. This is a source of small amounts of moisture entering the can that at the current time there isn't a solution. We don't believe that these areas along allow enough moisture to enter the can to cause a film to form.

Improper Mixing

With the changes in the prepolymer molecular size and viscosity, fill volumes and propellant blends, the effectiveness of the mixing methods currently being used may not result in a homogeneous mixture. It is important to evaluate the method you are using to mix the product to assure a homogeneous mix is being achieved. You may use pressure rated glass aerosols for testing so you can visually see the effectiveness of the mixing method used.

Heavy Metal Ion Contamination

Heavy metal ions are a catalyst for PU chemistry even at trace levels for OCF. Heavy metal ions can be introduced into the final product through:

1. The raw materials either from their manufacturing process or their source including being picked up from the ground (i.e., natural oil based raw material).

2. Released into the ingredients during processing by equipment such as pumps and piping. The newer the equipment or manufacturing plant the higher the chance of contamination.

Man heavy metal ions can have a synergetic effect when existing along with amine catalyst that can speed up the polymerization reaction during the production of OCF. Faster polymerization will result in:

1. Increased reaction temperature in the can.

2. Shortened time allowed between filling of A & B and mixing.
3. Increased potential for skinning.

4. Reduced shelf life.

In addition, even PPM levels of heavy metal ions can cause further reaction of an isocyanate group's NCO to:

1. Link with other NCO groups causing longer or cross-linked molecules.

2. Link with urethane linkage to form cross-linking.

3. Promote higher reactivity with water.

All these possibilities can lead to skin formation and/or shorten shelf-life.

It is important to know the level of heavy metal ions in your ingredients and their effect in the formula. It has been confirmed that some of the ingredients used in one component foam formulas contain trace amounts of metal contamination. Speak with your suppliers and ask for certification as to the level in your raw materials.

Improper Ingredient Selection

Obviously, selection of the proper raw materials is important. For instance, choosing between the following two types of surfactants is important.

1. OH containing.

2. OH blocked or low OH level.

For more sensitive products such as Mega Foam, OH blocked is preferred to prevent a crosslinking reaction between the surfactant and isocyanate which will result in larger molecules and a more sensitive product to water.

In conclusion, there are multiple possibilities that may result in the formation of a film on top of the prepolymer in a can of OCF. While enough isn't known at this time to pinpoint the cause for the renewed film formation phenomena, it is likely that there are multiple factors involved. While the valve is a point through which water can enter the can, the materials used to manufacture the valve have not changed enough over the years to be the only source of the problem. Effects of higher levels of DME in the gas blend, higher levels of propellant in the product and higher fill volumes in the can are being evaluated to determine their effect on the valves function.

It is important for formulators to understand the effect of the reactivity of the formulas and the effect of contaminants on the life of the product. All ingredients should be evaluated for possible contamination and specific limits set for heavy metal ions and water.

It is also important for fillers to insure proper storage of the components such that water contamination is not introduced and incoming raw materials meet proper specifications for moisture content and metal contamination.

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And last, but not least, it is important to test all new formulas with the packaging components to assure that the final product meets the markets requirements for function and shelf life.