



trans-1,2-dichloroethylene As an Additive for HFC-134a Foam Systems

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ABSTRACT

HFC-134a has been used as a zero ozone depletion potential (ODP) alternative for HCFC-141b in polyurethane foam applications. Between two major categories of zero ODP alternatives, hydrocarbons and HFCs, HFC-134a offers some advantages. It is non-flammable, widely available, and it has lower cost than other HFCs. It is an ideal choice for foam applications where non-flammability, volatile organic compounds (VOCs) and blowing agent costs are major issues. Yet, HFC-134a suffers from one significant drawback – it has limited solubility in polyurethane raw materials such as polyols. Although the issue can be alleviated by careful selections of polyols and use of coblowing agents such as water, there is a need to further improve the system.

trans-1,2-dichloroethylene is a liquid at room temperature (b.p. 48 °C). It has no ozone depletion potential* (ODP), and it has very low global warming potential (GWP) because it has very short atmospheric lifetime. Previously, we found that the addition of *trans*-1,2-dichloroethylene in HFCs based urethane foam formulations significantly improved the fire performance.

In this paper, we evaluated the effect of *trans*-1,2-dichloroethylene on the vapor pressure of several HFC-134a/polyol combinations. The results show that

the presence of *trans*-1,2-dichloroethylene can reduce the vapor pressure of certain HFC-134a/polyol blends. More importantly, the presence of *trans*-1,2-dichloroethylene allows one to reduce the levels of HFC-134a, therefore significantly reducing the overall vapor pressure of HFC-134a containing systems. Finally, the presence of *trans*-1,2-dichloroethylene can dramatically reduce the viscosity of HFC-134a/polyols blends, which are important for some applications.

INTRODUCTION

Among all hydrofluorocarbons or HFCs, HFC-134a is the most commonly used. It is widely used as a refrigerant, a foam blowing agent^[1,2] and a propellant in some applications. It is commercially manufactured by several producers around the world. With the phaseout of HCFC-141b, HFC-134a has become one of the most important zero ozone depletion potential (ODP) alternative blowing agents for the polyurethane foam industry. When a non-flammable blowing agent is necessary, HFC-134a is the least expensive option because it has relatively low cost and low molecular weight (therefore high blowing efficiency).

Because it has a low boiling point (-26 °C), and a relatively low solubility in polyurethane raw materials, HFC-134a containing polyol premixes or “B” side premixes tend to have a high vapor pressures. Consequently, a pressurized container is necessary when a high loading of HFC-134a is employed in the foam formulation unless HFC-134a is introduced as the third stream. Reducing the vapor pressure of HFC-134a containing polyol premixes is helpful in making HFC-134a more user friendly as a polyurethane foam blowing agent. Several approaches can be taken to decrease the vapor pressure of HFC-134a containing polyol premixes^[3,4]. The first one is to split a small fraction of the HFC-134a in the “A”

* Literature value. However, our internal calculation shows that *trans*-1,2-dichloroethylene has a negligible ODP. *Trans*-1,2-dichloroethylene should not be considered as playing a role in ozone depletion and is an illustration of the general conclusion of the WMO 2002 assessment stating the VSL chlorinated substances are not likely to have an impact on the ozone layer.

side (or polymeric MDI side). The second approach is to choose a polyol that gives the lowest vapor pressure. Previously, we found that there could be a significant difference in vapor pressure even though the polyols might appear to have similar characteristics (i.e., initiator and viscosity)^[4]. Finally, one can use water as a coblowing agent, therefore decreasing the amount of HFC-134a needed in the foam formulation. Previously, it was found that the addition of water does not adversely affect the overall vapor pressure of the polyol premixes^[4].

Despite this progress, it remains desirable to further reduce the vapor pressure of HFC-134a containing polyol premixes. Furthermore, the reduction of the loading of HFC-134a with water leads to higher viscosity for the HFC-134a containing polyol premixes. This is because the amount of water needed is only a small fraction of HFC-134a due to its low molecular weight (18 for water vs. 102 for HFC-134a). As a result, replacing HFC-134a with water reduces the vapor pressure, but increases the viscosity.

Thus, there is a need to develop an additive for HFC-134a containing polyol premixes or systems, in which the additives can reduce the vapor pressure of the HFC-134a containing polyol premixes, and furthermore reduce the viscosity of the polyol premixes as well. Previously, we found that trans-1,2-dichloroethylene or TDCE can significantly improve the fire performance of pentane and HFC based foams. Mobil 45 small scale fire test results show that the addition of 25 mole% of TDCE can significantly reduce the weight loss of foam samples during combustion^[5]. The presence of TDCE can also significantly improve the fire performance of HFC-245fa and HFC-365mfc based foams by reducing the initial weight loss rate and smoke production, according to cone calorimeter test results^[6].

In this paper, we study the effect of TDCE on the vapor pressure of HFC-134a containing polyol premixes, especially whether TDCE can be used to reduce the overall vapor pressure of the polyol premixes. In addition, we investigate the influence of TDCE on the viscosity of HFC-134a containing polyol premixes. Finally, we study the benefit of using TDCE in making HFC-134a foams, and determine the effect of TDCE on the properties of HFC-134a containing foams.

EXPERIMENTAL

Figure 1 shows a schematic diagram for an experimental setup utilized to determine vapor pressure of a foam blowing agent in polyurethane raw materials such as polymeric MDI and polyols. It consists of an incubator/refrigerator with an orbital shaker, a metal cylinder, a pressure transducer and a data acquisition system. The temperature inside the shaker is controlled within 0.1 °C with a uniformity of

0.2 °C. The system of interest, including polymeric MDI, polyol(s), blowing agents, catalysts, surfactants and other additives such as fire retardant(s) and TDCE is introduced into the metal cylinders step by step. A detailed description of the procedures was published earlier^[4]. Like before, stainless steel balls are added in the metal cylinder to facilitate mixing (through the orbital shaker).

The viscosity of polyol premixes was determined without the presence of HFC-134a, catalysts, surfactant and other additives. The only additive used here is TDCE. Polyester Polyol PS2352 and polyether polyol blends (Voranol 490/PS2352/Jeffol R-350x) with a predetermined amount of TDCE (0, 2, 4, 6 8 and 10 phpp) are blended, and then maintained in an incubator with temperature set at 25 °C for at least 16 hours. Then, the viscosity is determined using a Brookfield Digital Viscometer.

Foams were produced with an Edge-Sweets high pressure foam machine. To make HFC-134a containing foam, polyol premix or “B” side is made with a premix tank that includes a re-circulation pump and online static mixer. After all liquid “B” side components including polyol(s), catalyst(s), surfactant and additives such as TDCE are added into the premix tank; HFC-134a is introduced in the liquid form, as a separate stream, through an online static mixer. The polyol premix is continuously circulated during the addition of HFC-134a. Afterwards, the polyol premix is circulated for at least an additional 30 minutes before transferring into the tank in the Edge-Sweets high pressure foam machine.

Both “A” (with only polymeric MDI) and “B” sides are maintained in between 75-80 °F. The calibration (for “A” and “B” ratio as well as index) is performed using an online flowmeter because it is difficult to obtain accurate weight on the HFC-134a containing “B” side when HFC-134a loading is high (the “B” side will froth, and makes it difficult to weigh on a scale). The mixing pressures for the “A” and “B” side are both set at around 1500 psi (threshold). The mixture is poured into a tray, and it is allowed to rise without any constraint (free rise). The foam is allowed to cure for at least 24 hours prior to any testing.

To determine compressive strength of the polyurethane foams, we utilize ASTM D 1621. The sample size is about 2 inch x 2 inch x 1 inch (width x length x thickness), and the thickness direction is parallel to the rise direction. At least four samples are used for each formulation, and the results are the average of those samples.

For dimensional stability, we follow ASTM D 2126. The sample size is approximately 4 inch x 4 inch x 1 inch (width x length x thickness), and the thickness direction is parallel to the rise direction. For the hot, humid condition, we chose 70 °C and 97% of

relative humidity. For the cold condition, the samples are subject to $-40\text{ }^{\circ}\text{C}$. Three foam samples are used in each condition, and the results reported are the average of the three measurements.

Thermal conductivity, or k-factor, measurement (ASTM C518) was performed using a LaserComp Heat Flow Meter Instrument (Model Fox 314a). The mean temperature is $24\text{ }^{\circ}\text{C}$. The difference between hot and cold plates is kept constant at $24\text{ }^{\circ}\text{C}$. All samples are core foams with thickness of approximately 1.0 inch. Initial k-factors are taken within 24 hours after removing the foam skin with a band saw. For each formulation, at least two samples were tested, and the lowest k-factor was reported.

The following is a list of raw materials used in this study.

Voranol[®] 490 is a sucrose/glycerine initiated polyether polyol with 4.3 functionality and 490 hydroxyl number. It is available from Dow Chemical Company.

Voranol[®] RN490 is a medium functional polyether polyol with 4.6 functionality and 490 hydroxyl number. It is available from Dow Chemical Company.

Jeffol[®] R-350x is a polyether polyol available from Huntsman Polyurethanes.

PS 2352 (STEPANOL[®] PS 2352) is a polyester polyol produced by Stepan Company. Its hydroxyl number is 230-250.

PS 2412 (STEPANOL[®] PS 2412) is a polyester polyol produced by Stepan Company. Its hydroxyl number is 230-250.

PC-5 (POLYCAT[®]-5) is an amine catalyst produced by Air Products. Its chemical name is pentamethyldiethylenetriamine.

PC-41 (POLYCAT[®]-41) is a catalyst by Air Products.

B-8462 (TEGOSTAB[®] B8462) is a polysiloxane-polyether copolymer (or simply called silicone surfactant) produced by Goldschmidt Chemical Corporation.

HFC-134a (Forane[®] 134a) is 1,1,1,2-tetrafluoroethane available from Arkema Inc.

trans-1,2-dichloroethylene or TDCE (99+%) is available from Arkema Inc.

Mondur[®] 489 is a polymeric methane diphenyl diisocyanate (polymeric MDI) produced by Bayer Corporation.

RESULTS AND DISCUSSION

In small scale fire evaluations such as Mobil 45 and Cone calorimeter tests, *trans*-1,2-dichloroethylene or TDCE has proven to be effective in improving fire performance of pentane, HFC-245fa and HFC-365mfc based foams^[5,6]. To examine whether it is effective in reducing vapor pressure of HFC-134a in polyols, we determined the vapor pressure of HFC-134a/polyols in the presence of 0, 3.0 and 6.0 grams of TDCE in 50

grams polyol. At a HFC-134a loading equivalent to 0.2 mole (or 20.4 grams dissolved) in 100 grams of polyol, we found that TDCE is more effective in reducing the vapor pressure of HFC-134a/PS2412 than HFC-134a/Voranol RN490. The results, shown in Figure 2, indicate that the overall vapor pressure of HFC-134a/PS2412 is about 10 psi less with the presence of 6 grams of TDCE (compared to the one without any TDCE). At the same level of TDCE, the reduction of the vapor pressure of HFC-134a/Voranol RN490 is about 4 psi.

Additionally, TDCE can significantly decrease the vapor pressure of HFC-134a/polyol premixes by providing additional blowing power due to its low boiling point ($48\text{ }^{\circ}\text{C}$). Figure 3 shows vapor pressure of HFC-134a/water/polyols premixes with the presence of various levels of TDCE. In these experiments, the total amount of HFC-134a, TDCE and water is 0.276 mole. The level of water remains constant at 40 mole%, and the amount of TDCE changes from 0 to 50 mole% in 10 mole% increments. The polyol blend consists of 60% of Voranol[®] 490, 25% of Stepanol[®] PS2352 and 15% of Jeffol[®] R-350x. The results indicate that TDCE can be used to effectively reduce the vapor pressure of HFC-134a only systems with a steady reduction of overall vapor pressure as the level of TDCE increases. For example, we can reduce the vapor pressure of the overall system by about 15 psi (at $25\text{ }^{\circ}\text{C}$) when we change the "B" side composition from 60 mole% HFC-134a (with 40 mole% of water) to 40 mole% HFC-134a and 20 mole% TDCE (with 40 mole% of water). The vapor pressure decreases from about 72 psia to 57 psia. The vapor pressure of HFC-134a/TDCE (10/50) is only 25 psia. This experiment was performed by adding HFC-134a into a metal cylinder that had one atmosphere (or 14.7 psia) of air. In other words, the vapor pressure of HFC-134a/TDCE (10/50) would be less than one atmosphere if the air was removed prior to the addition of HFC-134a. The reduction of overall vapor pressure will make more HFC-134a more user friendly.

Water has been frequently used with HFC-134a to reduce vapor pressure of the "B" side system^[1,4]. Due to its low molecular weight, the absolute quantity of water used in the "B" side is small. Therefore, its effect as a diluent is greatly diminished. This results in high "B" side viscosity, which may cause processing problems. We found that TDCE can greatly reduce the viscosity of polyol or polyol blends. As shown in Figure 4, there is about 30% decrease in viscosity with only 2 phpp (part per hundred part polyol) of TDCE in the polyester polyol PS2352. The reduction in the viscosity is even more significant with 2 phpp of TDCE in a polyol blend consisting of 60% of Voranol[®] 490, 25% of Stepanol[®] PS2352 and 15% of Jeffol[®] R-350x. With 6 phpp of TDCE in PS2352, the viscosity is decreased by more than 50%. A similar reduction in viscosity can be achieved with

only 4 phpp of TDCE in the three component polyol blend.

To evaluate how TDCE affects processing and physical/mechanical properties of HFC-134a foam, we conducted a series of experiments with different levels of TDCE in the foam formulations. As listed in Table 1, the amount of water is kept constant at 40 mole%, while levels of TDCE change from 0, 20, 30 and 40 mole%. The total amount of HFC-134a/TDCE/water is kept constant at 0.276 mole, and the iso index is 120.

The degree of froth increases as the level of HFC-134a becomes higher, especially at 60 mole% of HFC-134a. For the formulation with HFC-134a/TDCE/Water (40/20/40), the dispensing of foam mixture is relatively smooth (with a creamy liquid rather than a violent froth). The surface of the free rise foam is also smooth. As shown in Table 2, there is a very significant increase in free rise core foam density (from 2.0-2.1 pcf to 2.5 pcf) when TDCE is completely removed from the formulation. This is probably due to a loss of blowing agent during the foaming process.

Initial thermal conductivity or k-factor (at 24 °C) results show that the addition of TDCE actually reduces or improves the initial thermal conductivity. The foam without TDCE has the highest initial thermal conductivity. This is due to the high loading of HFC-134a, which results in pinholes in the free rise foam. The pinholes, which are parallel to the rise direction (and heat flow direction), cause high thermal conductivity. The typical thermal conductivity of HFC-134a with high levels of HFC-134a should be obtained with molded rather than the free rise foam. The molded HFC-134a foam has lower (better) k-factor^[7]. Nevertheless, the results show a positive effect with the addition of TDCE.

The compressive strength of the free rise foam is also listed in Table 2. The results show those foams without TDCE have significantly higher compressive strength. However, it is impossible to conclude whether or not TDCE contributes to the drop in compressive strength because of the large differences in foam density (2.5 pcf vs. 2.0-2.1pcf). While TDCE is a very good solvent, and the plasticization effect of TDCE is anticipated to lower compressive strength, we expect that the presence of HFC-134a, a low boiling point blowing agent, can minimize the reduction of compressive strength due to the plasticization effect of TDCE.

The effect of TDCE on the dimensional stability is examined under both cold (-40 °C) and hot/humid (70 °C, 97% humidity) conditions, respectively. The results show that the foam samples containing up to 20 mole% of TDCE have good dimensional stability under both hot/humid and cold conditions. All foams have good dimensional stability under cold conditions, with average volume change around 1%. However,

the foams with 30% and 40 mole% of TDCE show a significant expansion under the hot and humid condition. It is noted that some individual samples showed much larger volume expansion than others (19% vs. 3%), suggesting that the foam samples are not uniform.

We plan to use the high pressure foam machine to produce more foam samples with improved quality and consistency for physical and mechanical property measurements. In addition, we plan to make molded foams to minimize the effect the pinholes on the thermal conductivity.

CONCLUSION

trans-1,2-dichloroethylene or TDCE is an effective additive in reducing vapor pressure of HFC-134a/TDCE/polyol premixes. Moreover, the addition of TDCE can dramatically reduce the viscosity of polyol or polyol blends. Finally, the presence of TDCE in HFC-134a based foam formulation can improve foam processing.

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REFERENCES

1. D. Rosbotham, J. Deschaght and A.K. Thomas, "HFC-134a – a zero ODP Option for Rigid Polyurethane Foam", Polyurethane Conference Proceeding, 17, 1992
2. D. C. Krueger and C. J. Reichel, "1,1,1,2-tetrafluoroethane as the Primary Blowing Agent for Rigid Polyurethane Foams Using Conventional Foam Mixing Equipment", 26, 1992
3. Ike Latham, "Factors Affecting the Solubility of Gaseous HCFC and HFC Blowing Agents", Polyurethanes Expo '96, p428, Las Vegas, Nevada.
4. J. Wu, D. Dillon and S. Eury, "HFC-134a and HFC-365mfc in Polyurethane Foam Applications", Utech 2003, Hague, Netherlands.
5. J. Wu, D. Dillon and R. Crooker, "Hydrochlorocarbons/Pentanes Coblown PIR Foams for Improved Fire Performance", Polyurethanes Conference Proceeding, 144, 2002
6. J. Wu, C. Bertelo and L. Caron, "*trans*-1,2-Dichloroethylene for Improving Fire Performance of Urethane Foam", Polyurethanes Expo, 454, 2003
7. J. Haworth, S. Sinaga, P. Irwin, D. Latham and R. Morgan, "New Developments with Appliance Rigid Foam Systems Utilizing Liquid and Gaseous Blowing Agents to Achieve Optimum Density,

Flowability, Cabinet Energy and Product Appearance”, Polyurethanes Expo '99, 427, 1999

BIOGRAPHIES

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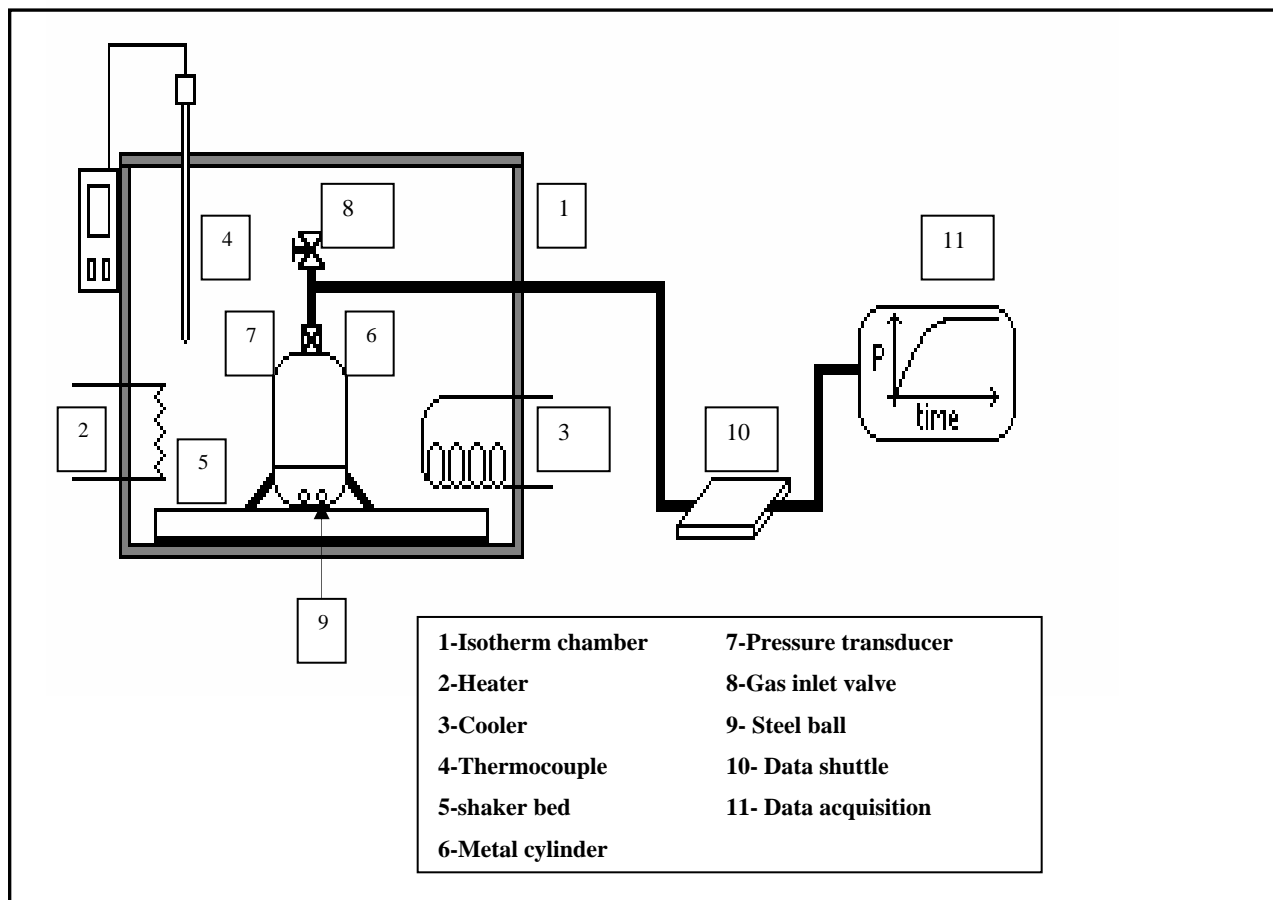


Figure 1. Schematic Diagram of Vapor Pressure Measurement

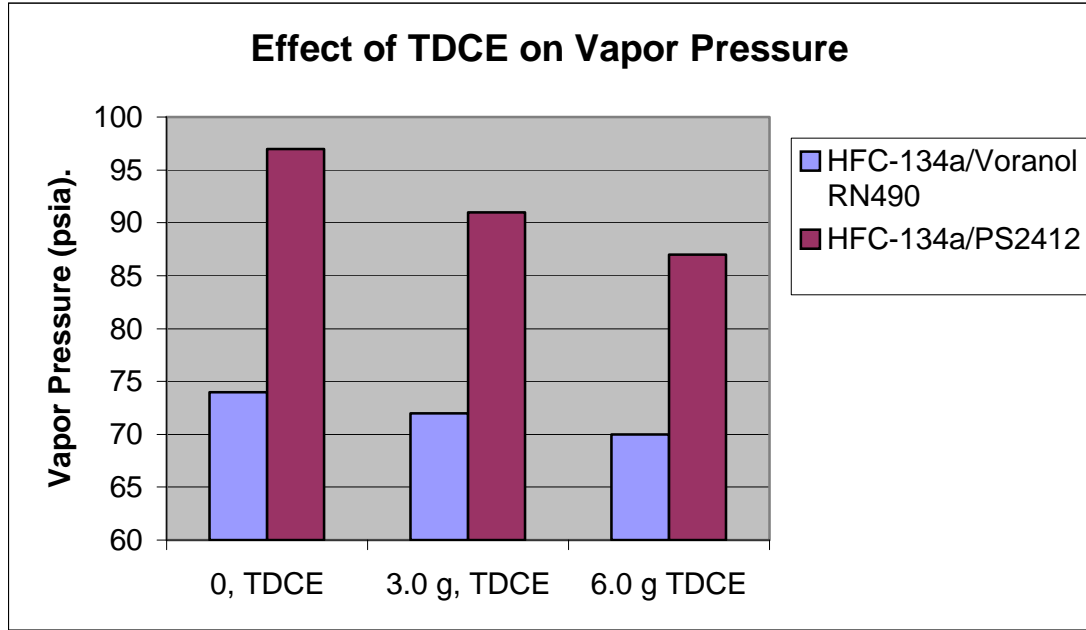


Figure 2. Effect of TDCE on the Vapor Pressure of HFC-134a/Polyol

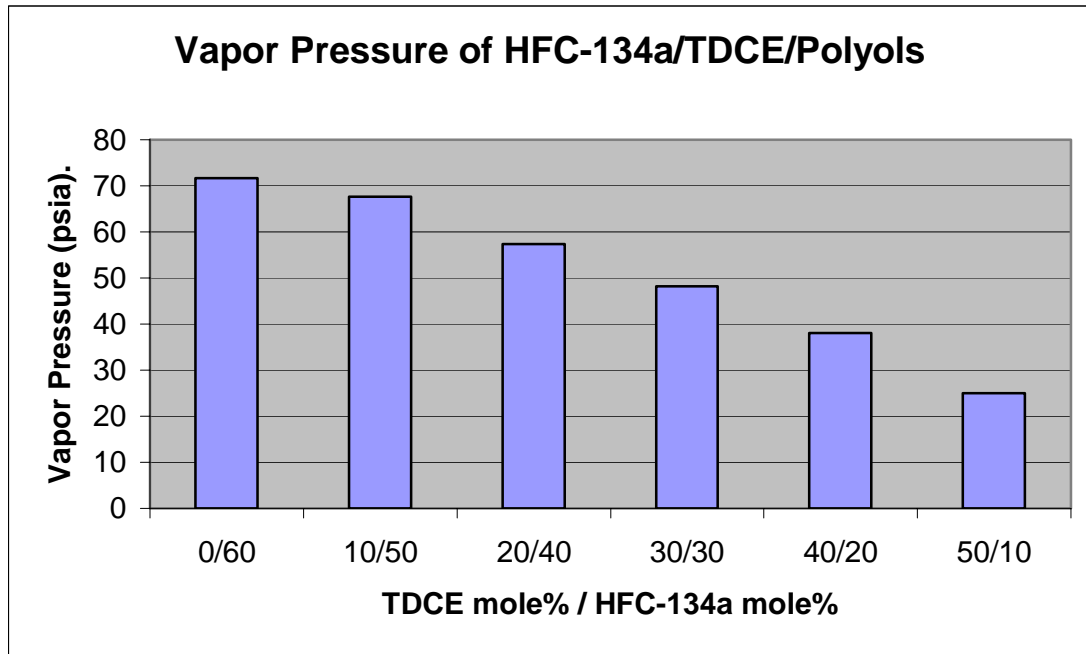


Figure 3. Vapor Pressure of HFC-134a/TDCE/Water/Polyols

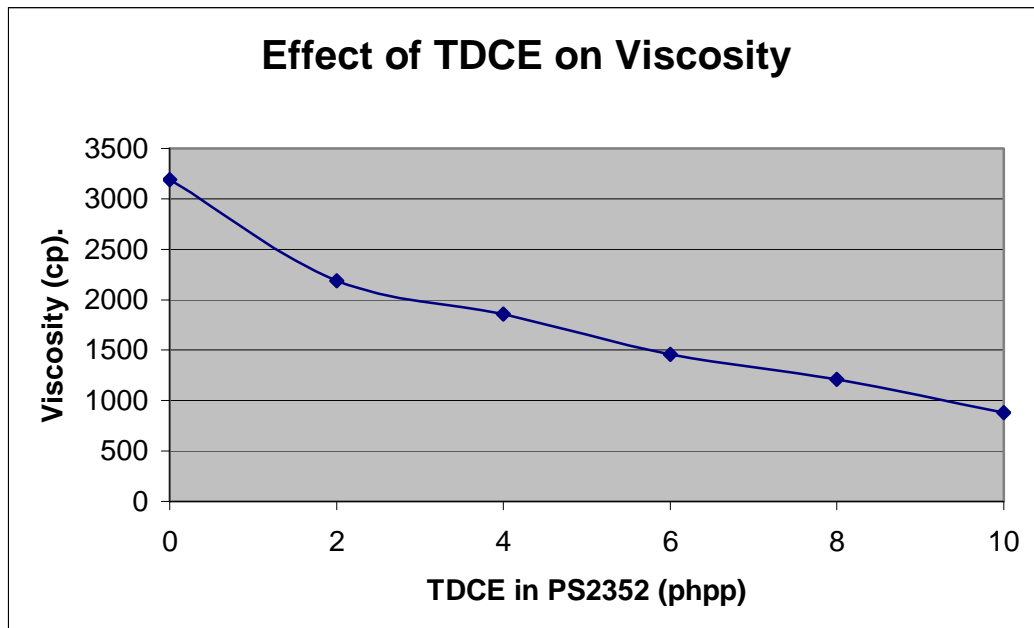


Figure 4. Viscosity of TDCE/PS2352 Blends

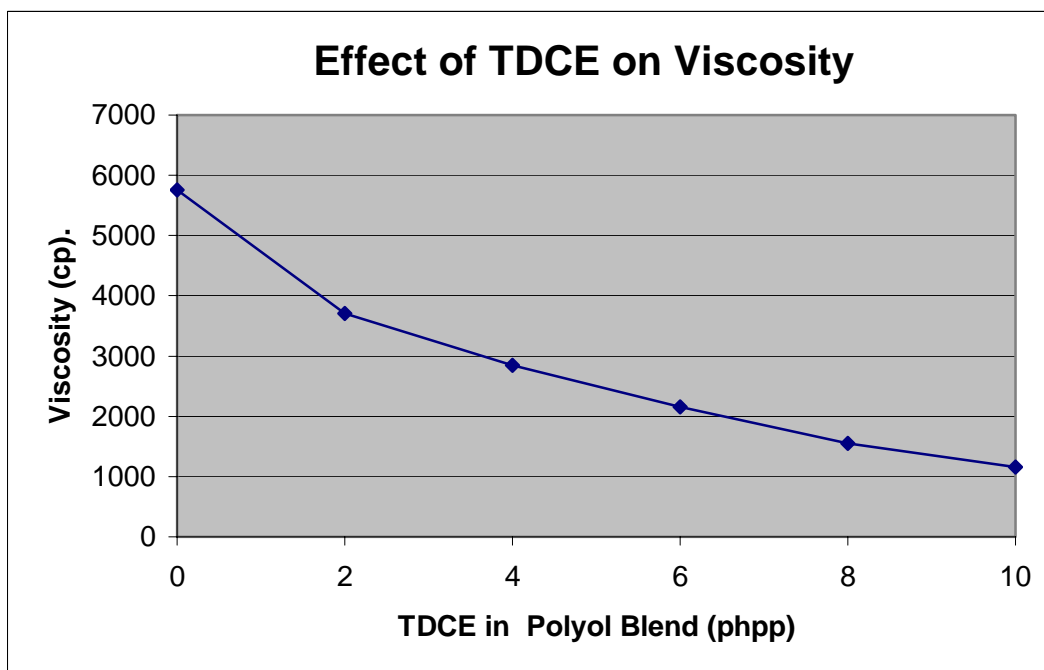


Figure 5. Viscosity of TDCE/Polyol Blends

Table 1. HFC-134a/Water/TDCE PUR Foam Formulations

134a/TDCE/Water (mole %)	60/0/40	40/20/40	30/30/40	20/40/40
Voranol [®] 490 ¹	60	60	60	60
STEPANPOL [®] PS 2352 ²	25	25	25	25
Jeffol [®] r-350x ³	15	15	15	15
POLYCAT [®] -5 ⁴	1.6	1.6	1.6	1.6
POLYCAT [®] -41 ⁵	0.6	0.6	0.6	0.6
TEGOSTAB [®] B- 8462 ⁶	2.0	2.0	2.0	2.0
Forane [®] 134a ⁷	16.9	11.3	8.4	5.6
TDCE	0	5.4	8.0	10.7
Water	1.99	1.99	1.99	1.99
Mondur [®] 489 ⁸	158.5	158.5	158.5	158.5
Iso Index	120	120	120	120

¹Dow Chemical Company; ²Stepan Company; ³Huntsman Polyurethane; ^{4,5}Air Products;
⁶Goldschmidt Chemical Corporation; ⁷Arkema.; ⁸Bayer Corporation

Table 2. Physical and Mechanical Properties of HFC-134a/Water/TDCE PUR Foams

134a/TDCE/Water (mole %)	60/0/40	40/20/40	30/30/40	20/40/40
Core Foam Density (pcf)	2.5	2.1	2.0	2.0
Initial k-factor (24 °C) Btu.in/ft².F.h	0.202	0.177	0.173	0.171
Compressive Strength (psi)	36 ± 3	24 ± 2	20 ± 1	25 ± 2
Volume change (%) 70 °C and 97% humidity at 1 week	1	1	5	7
Volume change (%) -40 °C at 1 week	1	1	1	0