Propylene Glycol Ethers for Ultrasonic Cleaning

by Prof. Bogdan Niemczewski[†]

Halogen solvents have been eliminated from surface cleaning processes, including ultrasonic cleaning, because of their harmfulness to human health (chlorinated solvents) and to the environment (freons). This has made it necessary to use other solvents which are often less effective but safer for people and the environment. To this end, propylene glycol ethers have long been known to the protective coating industry. A review of this type of solvent is presented here. Four proprietary examples were selected to assess their suitability for ultrasonic cleaning. Their behavior under ultrasonic conditions was compared with that for tetrachloroethylene which was commonly used in the past. A new method is described which makes such a comparison possible.

Introduction

After the signing of the Montreal Protocol, the removal of freons from use in industrial cleaning processes has had positive effects on the environment. At the same time, it has significantly reduced the simplicity and effectiveness of cleaning technology.[1-5] The situation has become even worse since the elimination of chlorinated solvents, because of their harmfulness to human health. Halogen solvents have a very important advantage over other solvents. They are non-flammable. In the case of ultrasonic cleaning however, there is still a need for flammable solvents. Certain halogen solvents, which have been proposed as replacements, are ecologically safe, but unfortunately are very expensive.[6] In this situation, there is a need for flammable solvents. It remains critical, however, that the solvent's flash point be as high as possible and in any case no lower than 55°C (131°F).[7]

An ultrasonic cleaning solvent should have the following characteristics:

1. It should effectively dissolve impurities.
2. It should not damage (etch) the surface being cleaned.
3. It should be safe (*i.e.*, non-toxic, non-explosive, minimally inflammable and ecologically sound).

In ultrasonic cleaning, there is a fourth feature, one that is very often forgotten. The solvent should also be able to transmit the physical phenomena, resulting from the ultrasonic action, which intensify the cleaning process. These physical effects are (1) ultrasonic cavitation and (2) solution agitation induced by the ultrasound radiation pressure.

Preliminary laboratory experiments have shown that some of the propylene glycol ethers may satisfy all the above mentioned conditions.[7,8] It would be useful to confirm these results on a larger industrial scale. This was the goal of this work.

The first two of the above mentioned conditions, i.e., the ability to dissolve impurities and not attack the substrate surface, have not been investigated. It was impossible because particular impurities and substrate surfaces have different properties. In general, it may be said that much better dissolution of impurities may be expected from the propylene glycol ethers than from freons. However their performance would be significantly worse than that of chlorinated solvents. The situation is quite different in regard to surface attack (except for metallic surfaces, which are not attacked by any of the solvents discussed here).

The subject of these studies was to assess the ability of propylene glycol ethers to induce cavitation and solution agitation as influenced by ultrasound radiation pressure. In order to make this assessment possible on an industrial scale, a novel methodology has been developed.

Numerous proprietary propylene glycol ethers have long been commercially available. The following four solvents were selected for this study:

1. Dipropylene glycol methyl ether (DPM),
$CH_3O[CH_2CH(CH_3)O]_2H$*

Nuts & Bolts: What This Paper Means to You

Because of health and environmental issues, halogen solvents, such as tetrachloroethylene (TCE), have been eliminated from surface cleaning processes, including ultrasonic cleaning. This has made it necessary to use other solvents which are often less effective but safer. Here, propylene glycol ethers were studied to see if they are suitable for ultrasonic cleaning and how they compare with the halogen solvents that they would replace.

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**Dowanol® DPM, The Dow Chemical Company, Midland, MI 48667.*

2. Dipropylene glycol dimethyl ether (DMM),
$CH_3OCH_2CH(CH_3)OCH_2CH(CH_3)OCH_3$**

3. Dipropylene glycol n-propyl ether (DPnP),
$C_3H_7O[CH_2(CH)CH_3O]_2H$*** and

4. Tripropylene glycol methyl ether (TPM),
$CH_3O[CH_2CH(CH_3)O]_3H$****

Certain physical properties of these products are given in Table 1.[9] The selection criteria were as follows:

1. A flash point no lower than 55°C (131°F)(Hazard Class A III or B III)
2. Complete (or as high as possible) solubility in water.

The last criterion must be explained. As can be seen in Table 1, all the propylene glycol ethers (except for the propylene glycol methyl ether (PM), $CH_3OCH_2CHOHCH_3$†) have a very low vapor pressure. This makes for difficulty in drying after cleaning. In practice, drying is only possible in vacuum dryers. In order to eliminate these difficulties it is advisable to add a hot water rinse after cleaning. Drying may then be carried out in the traditional way.

Experimental Procedure

Three 30-L (4 gal.) ultrasonic cleaner tanks were used in our experiments. The cleaners had ultrasonic transducers and generators operating at 25 kHz and 40 kHz, nominal frequencies generally used in industry. Two of the cleaner tanks (25 kHz and 40 kHz) operated at nearly equal electrical power of 350 W. The electrical power of the third cleaner (40 kHz) was twice as high, about 700 W. Each tank was filled with 22 L (3 gal.) of solvent, which was the working level for the tanks.

In order to measure the cavitation and agitation effects of the ultrasound radiation pressure, we used a radiometer designed by the author, allowing, unlike other radiometers, measurements in large tanks.[10] The radiometer consisted of a cone-shaped reflector suspended in the solvent and an electronic scale capable of automatically averaging the results over time (several seconds). Some modern electronic scales used for weighing small animals are so equipped. The reflector was hung on a special hook beneath the scales.

In the experiments described here, we used a duralumin reflector with the dimensions shown in Fig. 1. The reflector is comparatively large, and can detect force change induced by ultrasounds, on the order of several grams. The large reflector size plays an additional role. It simulates an object being cleaned, giving us more realistic conditions.

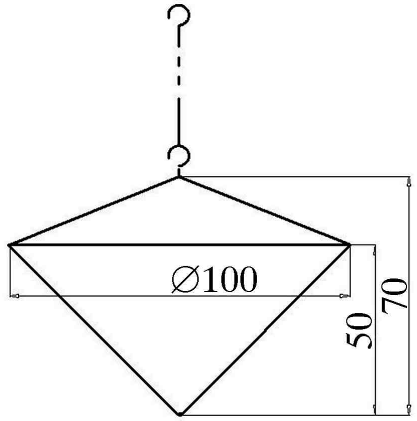

Figure 1—Schematic diagram of the radiometer reflector used in the experiments (dimensions in mm).

Table 1
Selected Physical Properties of Propylene Glycol Ethers

Chemical name	Chemical formula	Boiling point °C (°F)	Flash point °C (°F)	Specific Gravity (20°C)	Surface Tension (20°C) mN/m	Vapor Pressure (20°C) mbar	Solubility (20°C) in water g/100g	Solubility (20°C) of water in g/100g
Propylene Glycol Methyl Ether	$CH_3OCH_2CHOHCH_3$	120 (248)	31 (88)	0.92	28.3	11.5	∞	∞
Propylene Glycol n-Propyl Ether	$C_3H_7OCH_2CH(CH_3)OH$	149 (300)	48 (118)	0.89	25.7	2.3	∞	∞
Propylene Glycol n-Butyl Ether	$C_4H_9OCH_2CH(CH_3)OH$	171 (340)	63 (145)	0.88	27.9	1.1	5.5	18.5
Propylene Glycol Phenyl Ether	$(C_6H_5)OCH_2C(CH_3)HOH$	243 (469)	129 (264)	1.06	38.1	0.02	1.2	6.5
Dipropylene Glycol Methyl Ether	$CH_3O[CH_2CH(CH_3)O]_2H$	189 (372)	75 (167)	0.95	29.2	0.37	∞	∞
Dipropylene Glycol Dimethyl Ether	$CH_3OCH_2CH(CH_3)OCH_2CH(CH_3)OCH_3$	175 (347)	65 (149)	0.90	26.8	0.7	53	4.5
Dipropylene Glycol n-Propyl Ether	$C_3H_7O[CH_2(CH)CH_3O]_2H$	212 (414)	88 (190)	0.92	27.8	0.11	17.5	22.5
Dipropylene Glycol n-Butyl Ether	$C_4H_9O[CH_2CH(CH_3)O]_2H$	229 (444)	111 (232)	0.91	29.2	0.06	4.5	14
Tripropylene Glycol Methyl Ether	$CH_3O[CH_2CH(CH_3)O]_3H$	243 (469)	121 (250)	0.96	30.3	0.02	∞	∞
Tripropylene Glycol n-Propyl Ether	$C_3H_7O(C_3H_6O)_3H$	261 (502)	130 (266)	0.94	30.1	0.005	12.3	13.9
Tripropylene Glycol n-Butyl Ether	$C_4H_9OC_3H_6OC_3H_6OCH_2CHOHCH_3$	274 (525)	133 (271)	0.93	29.9	0.01	3	8.5

*** Proglyde® DMM, The Dow Chemical Company, Midland, MI 48667.*

**** Dowanol® DPnP, The Dow Chemical Company, Midland, MI 48667.*

***** Dowanol® TPM, The Dow Chemical Company, Midland, MI 48667.*

† Dowanol® PM, The Dow Chemical Company, Midland, MI 48667.

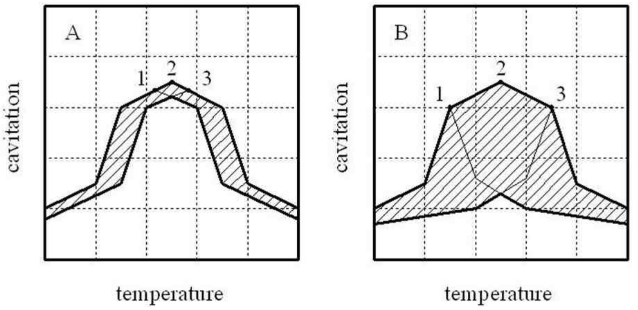

Figure 2—Areas occupied by sets of curves of cavitation vs. temperature (as an example sets of three curves) for (A) liquids having similar temperatures of maximum cavitation and for (B) liquids with a big scatter of these temperatures. The digits mark the points of maximum cavitation.

By means of a special tripod, the scales and reflector were placed above the cleaner tank so that the reflector was immersed in the center of the solvent volume. A scale, with a weighing capacity of 410 g and an accuracy of 0.01 g was used. Before each weighing, the scales were zeroed, with the ultrasound switched off.

A real-time averaging system was used to eliminate the influence of vibrations, which affected the stability of the readouts. The period of averaging was set at 8 s. After activating the ultrasound, the effect of the liquid pressing on the reflector, as induced by the radiation pressure and the so-called "quartz wind" or "acoustic wind", was read out on the scales as a negative number. The value was proportional to the intensity of the solvent movement under the influence of ultrasound.

Ultrasound causes the solvent temperature to rise. Moreover the temperature rise was intensified by heaters mounted in the cleaner

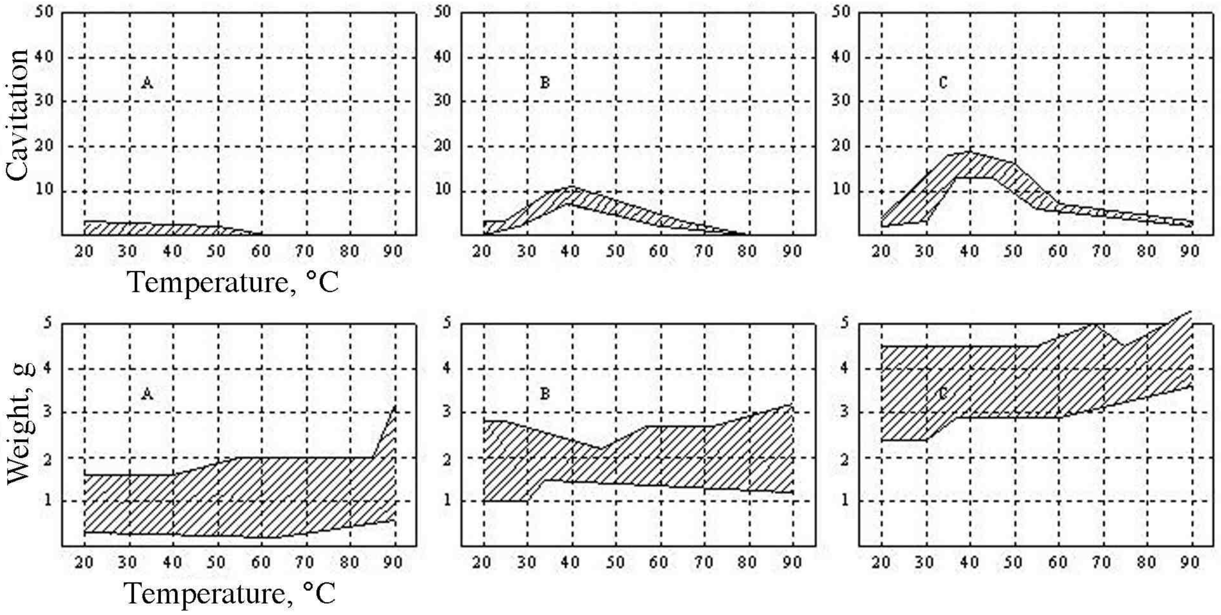

Figure 3—Results of measurements for tetrachloroethylene. The upper diagrams show areas occupied by all the curves (at different liquid levels) for average cavitation intensity of the liquid in the tank (measured in comparative units) versus temperature. The lower diagrams show areas occupied by all the curves (at different liquid levels) for the ultrasonic radiation pressure effects, measured as apparent weight loss of the radiometer reflector.
A. 25 kHz cleaner, 350 W; B. 40 kHz cleaner, 350 W; C. 40 kHz cleaner, 700 W

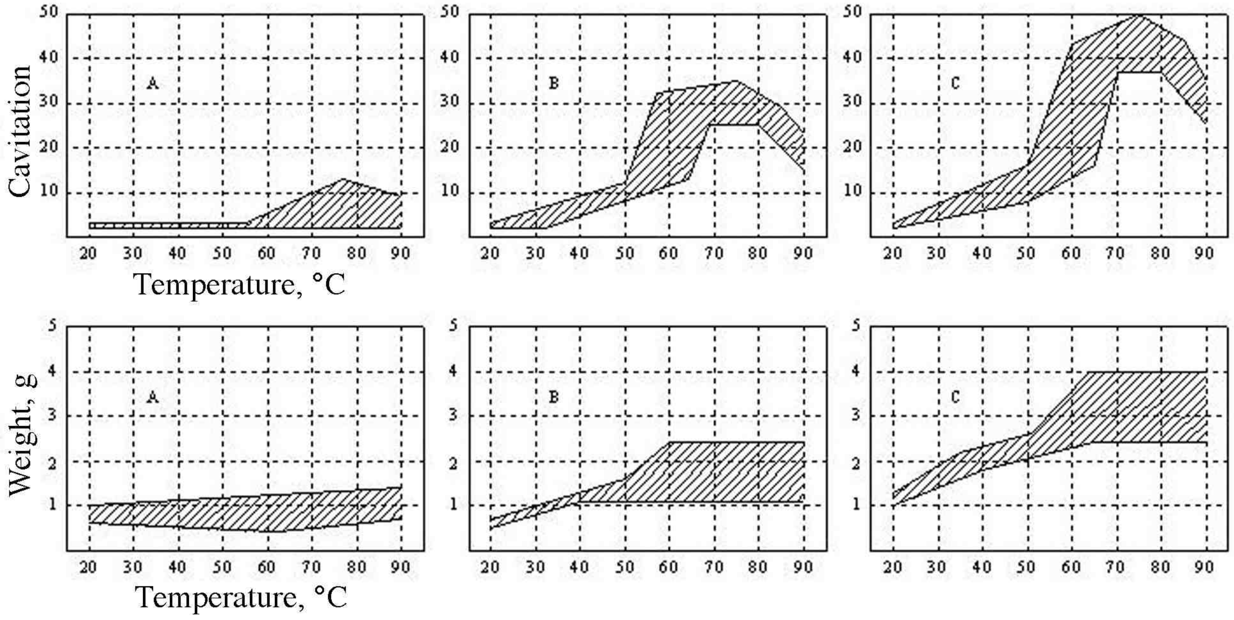

Figure 4—Results of measurements for dipropylene glycol methyl ether (Marking as in Fig. 3).

tanks. In order to draw a curve of the relationship between the force measurements and temperature, measurements were taken every 2 to 3C° (4 to 6F°). The curves had a shape of distorted sinusoids. One measurement cycle was not enough because the position of the sinusoid depended on ratio of the column of liquid in the cleaner to the length of the ultrasonic wave in the solvent. Therefore there were always seven measurement cycles taken, the height of the column of liquid (i.e., solution level) being lowered each time by 3 to 5 mm, so that the total change of the height of the column of liquid, from the first to last trial, was greater than 1/2 λ. After each measurement cycle the irregular sinusoid was shifted but returned nearly to its previous position after changing the height of the column of liquid by 1/2 λ. The area, occupied by all the curves drawn in one diagram, is characteristic of the intensity of solvent movement under the influence of ultrasound versus temperature.

In order to obtain similar curves characterizing cavitation, the author used a cavitation meter which used the principle of "cavitation white noise measurements."[11]†† There are various opinions on the credibility of this instrument, some of them contradictory. The controversy is related to the fact that its measurements relate to local and instantaneous cavitation intensities. Moreover they are affected by temperature and the liquid level in the tank. In the writer's opinion however, if the measurements are treated as comparative ones (e.g., for different liquids under like conditions) and in a statistical way (a large number of measurements taking into consideration temperature and height of the column of liquid), the results obtained are fully credible.

In all the experiments described here, cavitation was measured versus temperature at different liquid levels, in parallel with

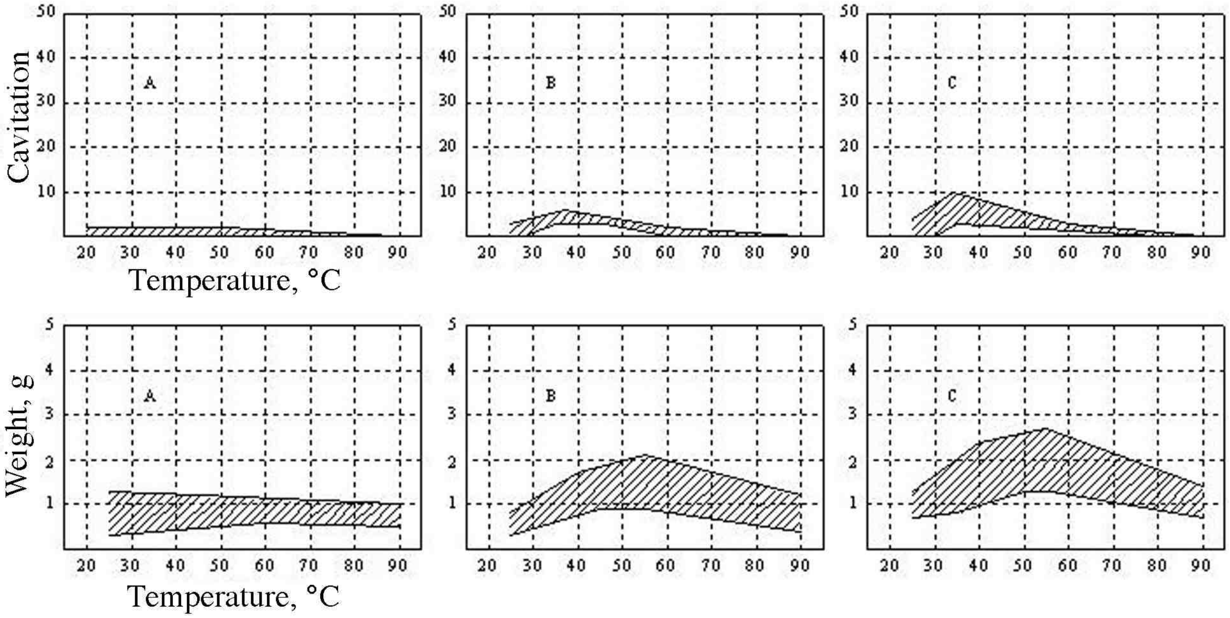

Figure 5—Results of measurements for dipropylene glycol dimethyl ether (Marking as in Fig. 3).

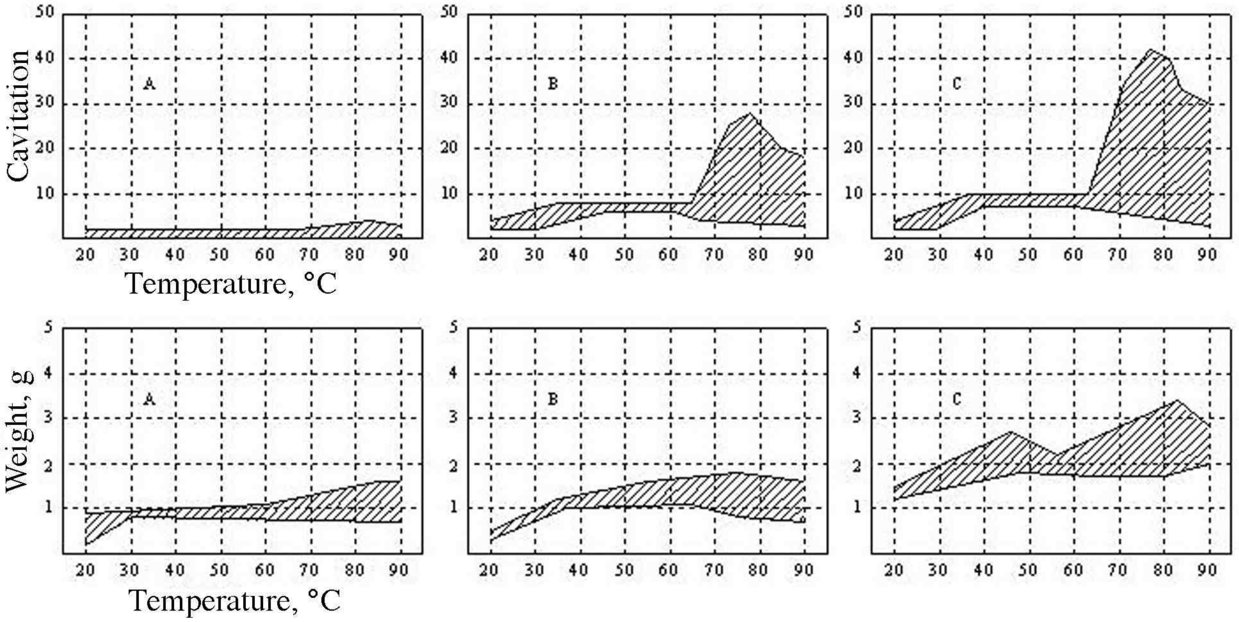

Figure 6—Results of measurements for dipropylene glycol n-propyl ether (Marking as in Fig. 3).

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†† Model 210 Cavitation Meter, Branson Ultrasonics Corp., Danbury, CT 06813.

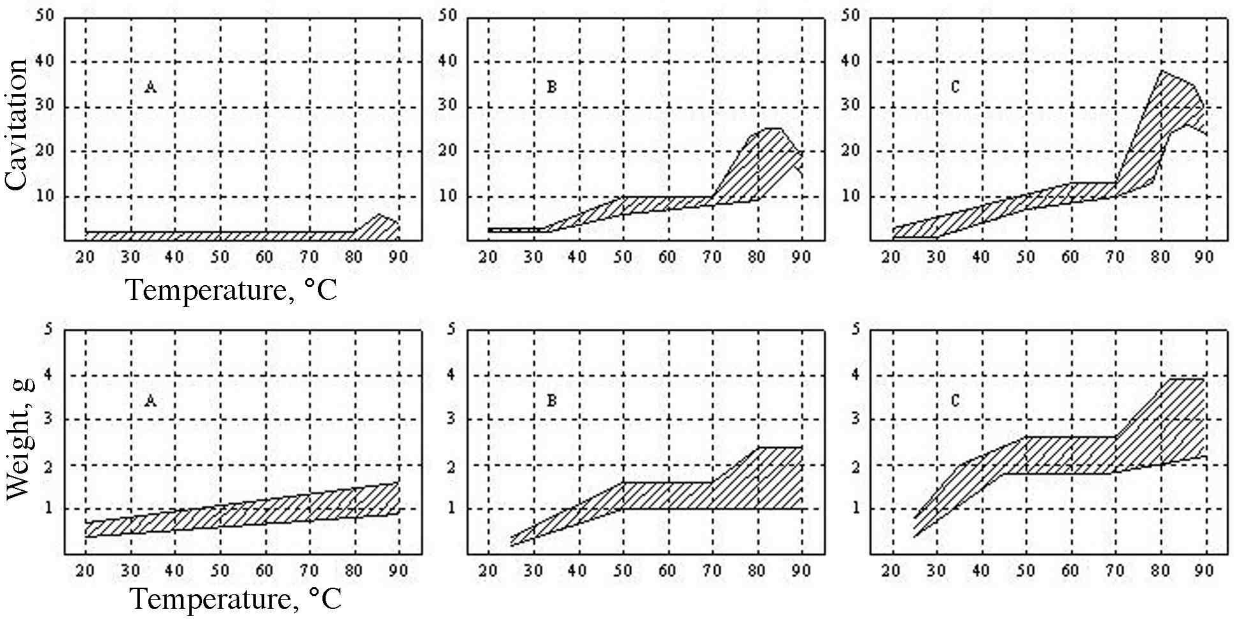

Figure 7—Results of measurements for tripropylene glycol methyl ether (Marking as in Fig. 3).

measurements of radiation pressure. The average cavitation intensity over the entire volume of the liquid in the tank was recorded. Local cavitation intensity peaks, which have been frequently observed in propylene glycol ethers, were not taken into consideration. The results of measurements, as for the radiation pressure, were presented as areas occupied by the sets of data curves for the same solvent but at different solution levels. It should be noted here that the maximum cavitation intensity of a given solvent depends not only on the height of the column of liquid but also that in some solvents, these maximum values are scattered over the temperature range of 10 or more Celsius degrees (>18F°). The areas occupied by the sets of curves for solvents having similar temperatures of maximum cavitation and by those having a large temperature scatter differ in size. A large area implies that the scatter is also large. This is illustrated schematically in Fig. 2.

Results and discussion

The results for the four propylene glycol ethers selected may be assessed only by comparison with similar results for a known reference widely used in ultrasonic cleaning. Tetrachloroethylene (TCE) was selected as that reference. Historically, it has been widely used in ultrasonic cleaning. Its ultrasonic radiation pressure and fairly good cavitation behavior is well known. Moreover, it has the highest boiling point among the halogen solvents used in ultrasonic cleaning.[12] At present, tetrachloroethylene is being eliminated from industry because it is harmful to human health, but its properties remain useful in the context of a research study reference.

The results of measurements of the cavitation and radiation pressure effects for tetrachloroethylene, carried out as described above, are presented in Fig. 3. The results for the four propylene glycol ethers are given in Figs. 4 thru 7. The areas marked with the letters A, B and C correspond to the 25 kHz cleaner (350 W), the 40 kHz cleaner (350 W) and the 40 kHz cleaner (700 W), respectively.

Notable in all the figures is a significantly lower cavitation intensity for the 25 kHz cleaner as compared to the 40 kHz cleaner at 350 W. This eliminates 25 kHz cleaners from consideration for cleaning in organic solvents. This is in accordance with our experience to date and with industrial practice. Doubling the electrical power in the 40 kHz cleaner resulted in a 1.5 to twofold increase in cavitation intensity, which is essential for cleaning.

The maximum cavitation intensities (40 kHz) in dipropylene glycol methyl ether (DPM), dipropylene glycol n-propyl ether (DPnP) and tripropylene glycol methyl ether (TPM) are more than double the values for tetrachloroethylene (TCE). They were observed, however, at much higher temperatures than in the case of TCE. In view of having better solubility of impurities at higher temperatures, the fact that the maximum cavitation appeared at higher temperatures would be very advantageous were it not for the fact that in case of DPnP and especially DPM, the point of maximum cavitation is dangerously close to the flash point. This means that in practice it is necessary to run the cleaning process at temperatures slightly lower than the temperature of maximum cavitation. This is so because it is recommended that one operate at a certain level below the flash point (about 15 Celsius degrees [27F°]). This is not a factor with TPM. On the other hand, the maximum cavitation in dipropylene glycol dimethyl ether (DMM) is significantly different. It appears, as with TCE, at temperatures around 40°C (104°F). On the other hand, its value is half of that for TCE. This fact and comparatively low radiation pressure intensity seem to eliminate DMM as a solvent for ultrasonic cleaning.

The charts illustrating cavitation in DPnP are similar to those presented in Fig. 2b. The points of maximum cavitation are widely scattered. The cavitation intensity of this solvent is very much dependent on the solvent level in the cleaner tank.

As can be seen in the diagrams, the 25 kHz cleaners are also explicitly worse than at 40 kHz as regards their ability to induce solvent movement. Further, a doubling of the electrical power in the 40 kHz cleaner in this case intensifies the effect by a factor of 1.5 to 2 (except for DMM).

In contrast to the cavitation effects, the effects of radiation pressure in propylene glycol ethers are smaller than what is observed in TCE. The best, in this respect, is DPM. The effects observed were at a level of about 70% of the effects observed in TCE at a higher power and at a level of 80% at lower power, but only at temperatures above 60°C (140°F). Similar effects are seen with TPM, at temperatures above 80°C (176°F).

In all four propylene glycol ethers, the highest radiation pressure effects were observed at temperatures close to those in which the highest cavitation was observed. This is a positive outcome, because it explicitly points to the temperatures where ultrasonic cleaning in these solvents will be most effective. The temperatures are as follows:

DPM - About 75°C (167°F) (Because of the flash point it is recommended that this temperature be lowered to about 60°C [140°F])

DPnP - 73 to 83°C (163 to 181°F) (Because of the flash point it is recommended that this temperature be maintained at the lower end of this range.)

TPM - About 80°C (176°F).

Conclusions

These experiments have shown that three of the selected propylene glycol ethers, dipropylene glycol methyl ether (DPM), dipropylene glycol n-propyl ether (DPnP) and tripropylene glycol methyl ether (TPM), are suitable as solvents for ultrasonic cleaning if their ability to dissolve a given impurity is adequate.

The conditions that must be satisfied are (1) using a 40 kHz cleaner (not 25 kHz) and (2) running the process at a high temperature (as shown above for each solvent). Under these conditions, these solvents produce a very high cavitation intensity and fairly intense agitation under the influence of ultrasound.

The method of assessing the suitability of solvents for ultrasonic cleaning described here may be useful in evaluating other solvents.

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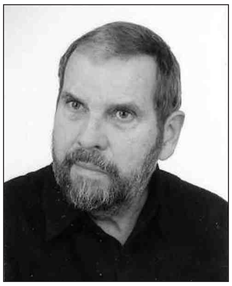
About the Author



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