

# Introducing Pemulen® Polymeric Emulsifiers

Pemulen® polymeric emulsifiers are predominantly high molecular weight polyacrylic acid polymers. These novel primary emulsifiers have a small oil-loving (lipophilic) portion in addition to a large, water-loving (hydrophilic) portion.

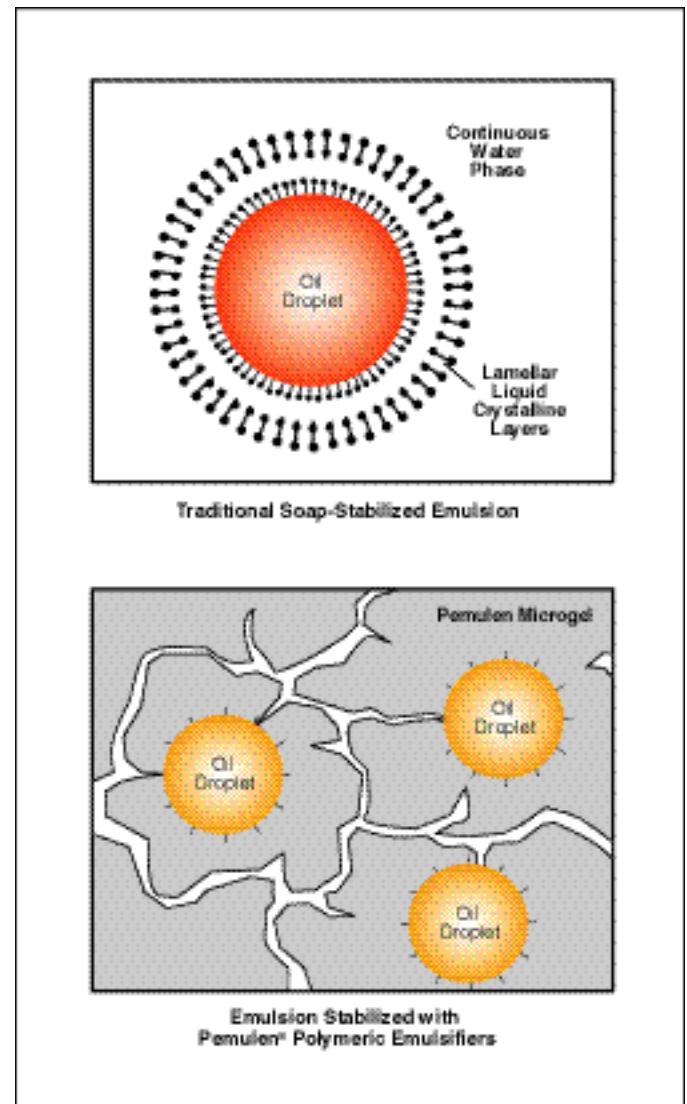
This chemical structure allows these copolymers to function as primary emulsifiers in oil-in-water emulsions. Whereas Carbopol® water soluble polymers have proven useful as secondary oil-in-water (o/w) emulsion stabilizers, Pemulen polymers can actually form o/w emulsions. The lipophilic portion adsorbs at the oil-water interface, and the hydrophilic portion swells in the water forming a gel network around oil droplets to provide exceptional emulsion stability to a broad range of oils.

## How Pemulen Polymeric Emulsifiers Work

Traditional ionic or non-ionic surfactants stabilize oil-in-water emulsions principally by adsorbing and forming lamellar liquid crystalline layers at the emulsion interface requiring usage levels of 3–7% of surfactant. The hydrophilic-lipophilic balance (HLB) of the oil phase and surfactant must be carefully matched to insure good emulsion stability. Often polymeric hydrocolloids, such as Carbopol resins, are added to increase the stability of the oil-in-water emulsions by thickening and adding yield value or structure to the water phase.

Emulsions created with very low levels of Pemulen emulsifiers are highly stable. Oil droplets are protected and held in place as a result of the very high yield aqueous gel around each oil droplet. On forming o/w emulsions, Pemulen molecules form an adsorbed gel layer around each oil droplet, with the hydrophobic portions of the polymer anchored in the oil phase. Thus, when two oil droplets approach each other, a physical repulsive force is generated by the presence of these adsorbed gel layers. This mechanism is represented in Figure 1.

Figure 1



## Benefits of Pemulen Polymeric Emulsifiers

Pemulen polymeric emulsifiers<sup>1</sup> are novel oil-in-water (o/w) emulsifiers which provide numerous benefits to emulsions prepared with them:

**Universal Emulsification** – Pemulen emulsifiers are water soluble polymers that readily anchor at the oil-water interface independent of oil type. Pemulen emulsifiers do not depend on building liquid crystalline structures to provide emulsion stability, therefore, they can be used with virtually any oil phase, regardless of the oil phase HLB or temperature of emulsification. Oil-in-water emulsions have been made with many non-reactive, non-ionic oil types, including mineral oil, volatile silicone oils, aromatic oils, fatty ethers or esters, and hydrocarbons/waxes. Oils can be emulsified at room temperature, and fats or waxes are emulsified at their molten temperature.

**Excellent Stability** – A broad range of emulsions have remained stable in the bottle for years, even at elevated temperatures of 40°C. (See Figure 2) These emulsions are also stable to repeated freeze-thaw conditions.

**Low Irritancy/Low Usage Levels** – Due to their hydrogel nature and highly efficient properties, typical usage levels of only 0.1-0.3% of a Pemulen emulsifier are required to replace 3-7% of traditional surface active emulsifiers which can be irritating.

**Rapid Release of the Oil Phase** – Emulsions created with Pemulen emulsifiers have a triggered release mechanism. The acrylic hydrophilic portion of the Pemulen emulsifier hydrogel instantly deswells upon contact with the surface characteristics and salt content common on skin. The oil phase is released and provides immediate coverage of the substrate, eliminating the lengthy lag time seen in traditional o/w emulsions. (See Figures 3-6)

In traditional emulsions, lamellar liquid crystals, comprised of oil, water, and surfactant, retard the rate of deposition of the oil phase to the substrate. These liquid crystal structures persist for up to ninety minutes after application. The liquid crystal structures may be observed by polarized light microscopy. The time lag from application to the formation of the continuous oil phase is caused by the slow evaporation of the water phase from the liquid crystal structures.

<sup>1</sup> CTFA name: Acrylates/C10-30 Alkyl Acrylate Cross-Polymer. Pemulen resins are polymerized in an ethylacetate-cyclohexane mixture. This solvent mixture is environmentally and toxicologically preferred to benzene and chlorinated solvents.

Figure 2  
Median Droplet Sizes of Emulsion Gels Prepared by Different Methods in Relation to Storage Time

### At Room Temperature

	Median Droplet Size (µm)			
	After Preparation	After 1 month	After 3 months	After 6 months
Manual Process	300 (100-1000)	250 (100-1000)	300 (100-1000)	300 (100-1000)
Mechanical Process	20 (10-30)	25 (10-40)	25 (10-40)	25 (10-40)

### At Elevated Temperature (40°C)

	Median Droplet Size (µm)			
	After Preparation	After 1 month	After 3 months	After 6 months
Manual Process	300 (100-1000)	300 (100-1000)	300 (100-1000)	300 (100-1000)
Mechanical Process	25 (10-40)	25 (10-40)	25 (10-40)	25 (10-40)

Source: Bremecker, Klaus et al: In *Die Pharmazeutische Industrie* 54; 182-185; (1992)

**Oil Phase Will Not Re-Emulsify** – When formulated with little or no surfactant, the oil phase in a Pemulen emulsion can spread rapidly and cannot re-wet. Waterproof emulsions are therefore easily prepared. In traditional emulsions, upon final evaporation of the oil phase, the oil layer contains high concentrations of surfactants,<sup>2</sup> rendering the oil phase readily re-emulsifiable.

**Simplifies Emulsion Formation Procedures** – Stable emulsions can be formed by the stepwise addition of oil phase ingredients to the water phase at any temperature, including ambient room temperature, at which point all ingredients are liquid. Economies may be derived from the elimination of heating and cooling cycles during manufacture.

**Effective O/W Emulsions at Low Loadings** – Due to the immediate availability of the active oil phase using Pemulen emulsifiers, the equivalent efficacy at reduced oil or solvent levels may be seen.

<sup>2</sup> H. Tsutsumi, T. Utsugi and S. Hayashi, *Journal of the Society of Cosmetic Chemistry*, 30, 345, 1979.

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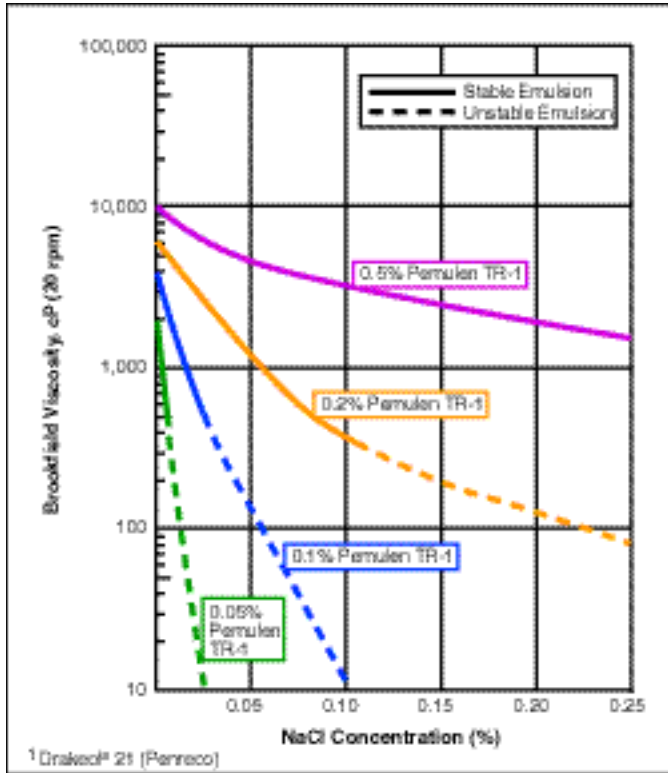
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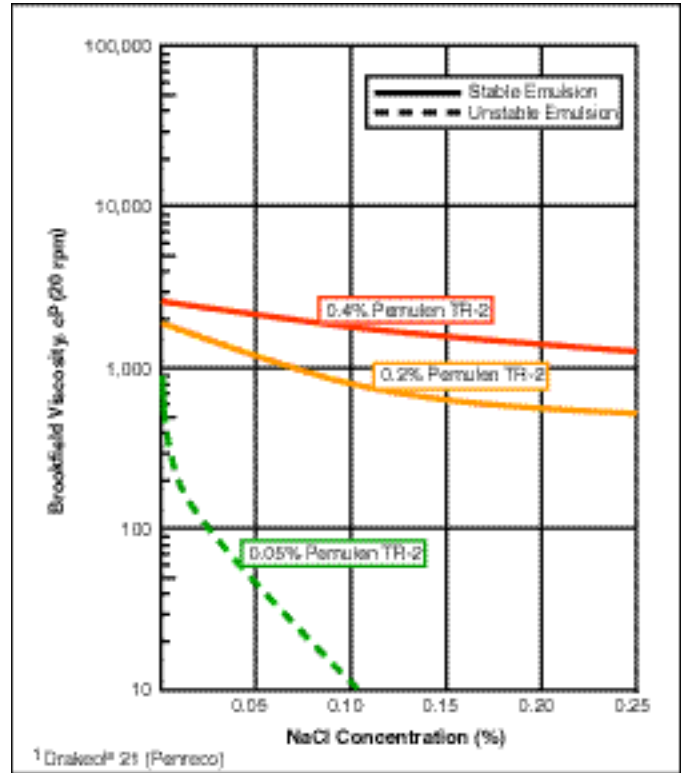
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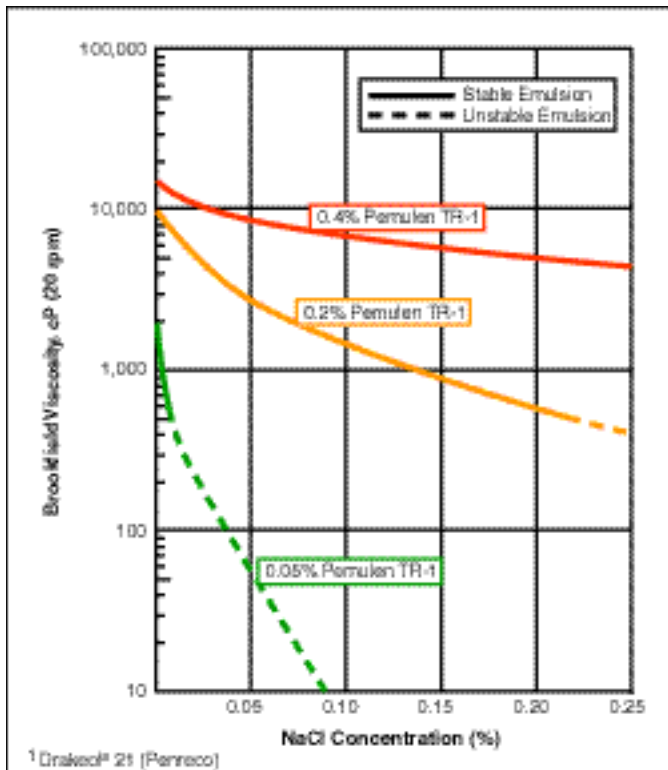
**Figure 3**  
 Effect of NaCl Concentration on Emulsion Viscosity and Stability for Pemulen TR-1 and 5.0% Mineral Oil<sup>1</sup> O/W Emulsion [pH = 7.0 ± 0.2 neutralized with 18% NaOH]



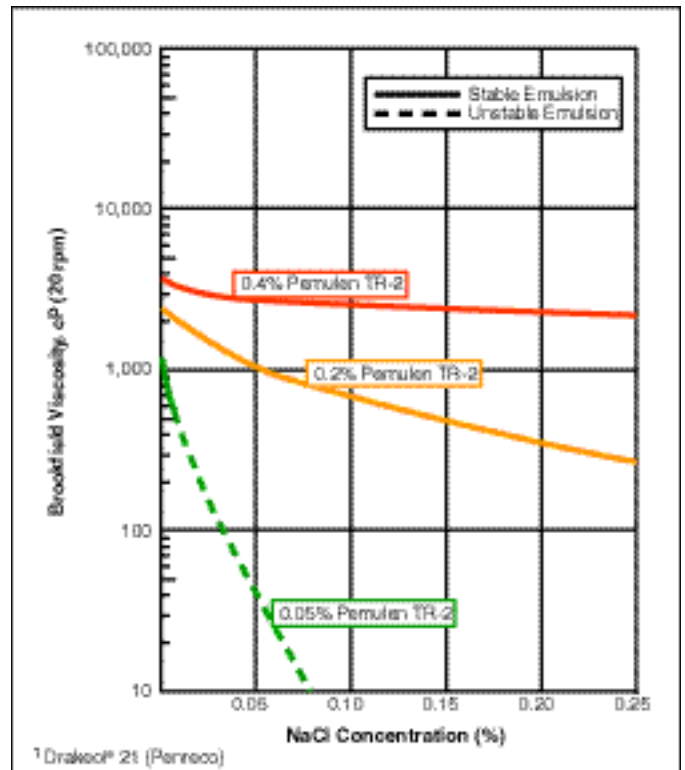
**Figure 5**  
 Effect of NaCl Concentration on Emulsion Viscosity and Stability for Pemulen TR-2 and 5.0% Mineral Oil<sup>1</sup> O/W Emulsion [pH = 7.0 ± 0.2 neutralized with 18% NaOH]



**Figure 4**  
 Effect of NaCl Concentration on Emulsion Viscosity and Stability for Pemulen TR-1 and 30.0% Mineral Oil<sup>1</sup> O/W Emulsion [pH = 7.0 ± 0.2 neutralized with 18% NaOH]



**Figure 6**  
 Effect of NaCl Concentration on Emulsion Viscosity and Stability for Pemulen TR-2 and 30.0% Mineral Oil<sup>1</sup> O/W Emulsion [pH = 7.0 ± 0.2 neutralized with 18% NaOH]



**Potential Reduction of Application Frequency** – Since the oil phase is not readily re-emulsifiable, the active oil phase remains in place longer, possibly minimizing the need for reapplication.

**New Product Forms Are Now Possible** – Stable, low viscosity, sprayable emulsions and translucent macroemulsions (o/w emulsions with oil drops with diameters greater than 0.5 mm) can now be prepared.

## Formulation Guidelines

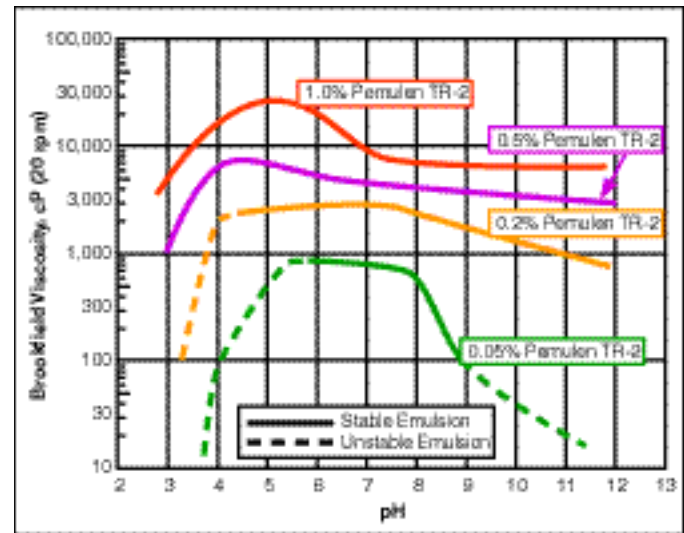
**Compatibility** – Pemulen polymeric emulsifiers are compatible with a broad range of nonionic or slightly ionic water soluble materials. High levels of electrolytes will prevent the normal swelling of the hydrophilic portion of the molecules, and emulsion creaming may result. Cationic species will complex with Pemulen resins, although low levels of many cationic materials are compatible and effective as spreading and wetting agents. (See TDS-124 for more details.)

**Particle Size** – Pemulen resins are capable of producing extremely stable macro emulsions, even at large average oil particle sizes (approaching 1-2 millimeters diameter). For aesthetic reasons it is often desirable to produce small particle size (1-5 micron) emulsions having a high degree of whiteness, opacity and creamy appearance. Low levels (0.1-0.4%) of liquid medium HLB (8-12) nonionic surfactants such as a nonyl phenoxy-poly (ethyleneoxy) ethanol (Igepal Co-530, Rhone-Poulenc) or sorbitan monooleate (Span 80, ICI) are very effective additives for achieving these particle sizes. High shear mixing may reduce particle size. In-line non-recycling homogenizers and colloid mills should be used in controlled moderation to avoid degradation of the polymer's hydrophilic gel network which contributes to emulsion instability.

**Neutralization** – Pemulen resins are mild acidic polymers and function best when neutralized with a suitable water soluble base to the desired pH (pH = 4-8). (See Figure 7) Inorganic alkali bases such as sodium hydroxide, potassium hydroxide or ammonium hydroxide are effective neutralizing agents. In addition, organic amine bases such as triethanolamine, tromethamine, aminomethyl propanol and tetrahydroxypropyl ethylenediamine are particularly suitable due to their relative mildness and low equivalent weights.

**Moderation of Breaking Upon Application** – Emulsions prepared with Pemulen as sole emulsifier or thickener release the oil phase very quickly upon application. This effect may not be desirable in some applications. To decrease the rate of emulsion breaking and liquefying, the use of a low level of a slightly surface active film former is recommended.

**Figure 7**  
Effect of pH on Pemulen® TR-2 Emulsion Viscosity  
[5% Mineral Oil Emulsions Neutralized with 18% NaOH Solution]



Hydroxypropyl methylcellulose at a 0.10% concentration, or Poloxamer 181, 182 or 183 at 0.5% concentration are very effective. Formulations which contain some surfactant resulting in a relatively small particle size and higher phase volume of oil (e.g. >30%) may not require such an additive.

**Structuring/Body Agents** – Use of compounds that typically structure o/w emulsions at the interface, such as cetyl and stearyl alcohols and partial glycerides should be limited. Undesirable, highly cohesive textures often result, and the lyotropic liquid crystals formed by cetearyl alcohols will delay the release of the oil phase for emollient properties or protection behavior.

The following is a sample of products that have been successfully emulsified in water with 0.4% or less Pemulen TR-2:

- Cyclomethicone
- Linseed Oil
- Mineral Oil
- Mink Oil
- Napthenic Oil
- Oleic Acid
- Perflorinated Oils
- Pine Oil
- Silicone Fluid
- Tallow
- Tung Oil

**Thickening** – Pemulen polymeric emulsifiers do provide thickening of o/w emulsion formulations. If additional body or thickening is desired, Carbopol resins are recommended, typically at 0.2-0.6% concentrations.

## Emulsification Procedure

Pemulen emulsifiers are adaptable to a variety of emulsion preparation methods. Pemulen powder is most easily dispersed in room temperature oil. Combine with the water phase containing the neutralizing alkali or amine using rapid, turbulent mixing action.

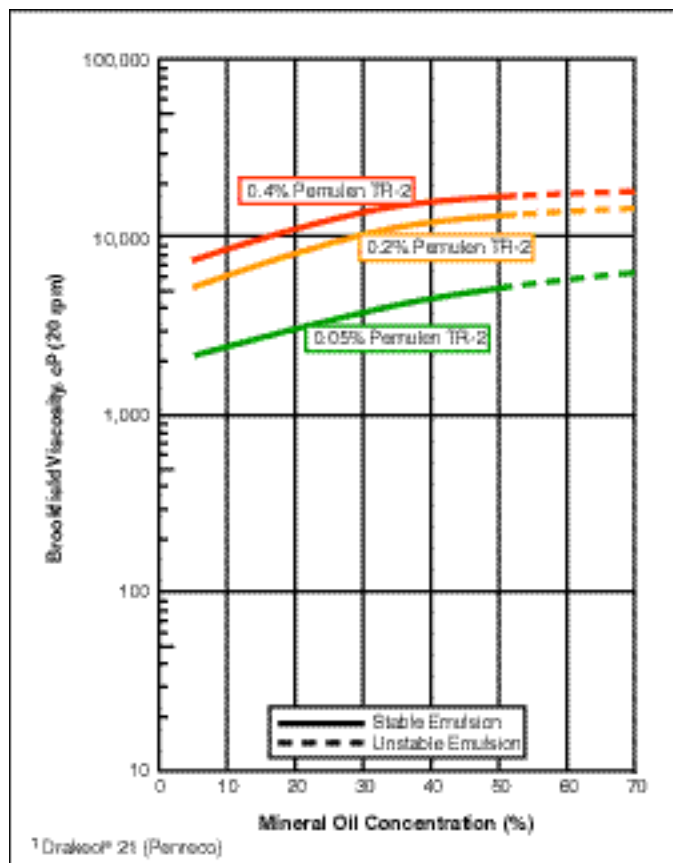
In the presence of some polar oils (aromatic or dicarboxylic acid esters) or molten oils above 60°C, Pemulen may physically plasticize, hindering stable emulsion formation. Dispersing Pemulen directly into the water in these cases will result in smooth, stable emulsions.

## Pemulen Type Selection

In general, the selection of Pemulen type is based upon the level of oil to be emulsified:

Pemulen TR-1 is a versatile polymeric emulsifier which can emulsify up to 30% oil by weight, within a pH range of 4-5.5, and up to 20% oil over the pH range of 3-11. (See Figure 8) While Pemulen TR-1 thickens the water, Carbopol resins should be used with Pemulen TR-1 to provide greater thickening properties where higher viscosity emulsions are required.

Figure 8  
Effect of Mineral Oil Concentration on Pemulen TR-1  
Emulsion Viscosity and Stability  
[Neutralized to pH 5.5 ± 0.2 with 18% NaOH]



Pemulen TR-2 contains the higher level of hydrophobic groups and can emulsify the highest levels of oil (up to 60-80% by weight) within a pH range of 4-5. (See Figures 9 and 10) Pemulen TR-2 is highly effective at levels below 0.4%, providing a low-viscosity emulsion particularly suitable for application via spray mechanism.

## Relative Base Strength Parts Required Per One Part Pemulen

(Neutralized to an approximate pH of 6.0-7.0)

Sodium Hydroxide (18% solution).....	0.5
Potassium Hydroxide (18% solution).....	0.5
Ammonium Hydroxide (28% solution).....	0.3
Triethanolamine (TEA).....	2.0
Tromethamine (2-amino	
2-hydroxymethyl-1,3-propanediol).....	2.0
Aminomethyl propanol (AMP).....	1.5
Tetrahydroxypropyl ethylene diamine.....	2.0

## Indirect Method

1. Disperse the Pemulen polymeric emulsifier in the oil phase until the powder is wetted in the oil.
2. Add the oil phase (containing Pemulen) to the water phase, containing the neutralizing alkali, under vigorous (800-1500 rpm) agitation. Do not use in-tank homogenizers.
3. Pemulen will swell rapidly in water causing a swift build of viscosity and the formation of a creamy emulsion. Continue with vigorous agitation for 15-20 minutes.

## Direct Addition Method

1. Disperse the Pemulen polymeric emulsifier by sifting slowly into rapidly agitating water. An educator or powder disperser may be used to speed dispersion. Foaming will occur during this step.
2. Continue agitation, pour in the oil phase, and neutralize with a suitable base.
3. Use rapid (800-1200 rpm) mixing to reduce particle size and obtain a glossy product. Controlled homogenization may be useful, but viscosity variation could result from high shear.

NOTE: Liquid nonionic surfactant (HLB 8-12) in a concentration of 0.1-0.4% may be added to the oil phase to reduce the size of the oil droplets, and improve the creamy appearance of the emulsion.

## Testing for a Stable Emulsion

After you have made an emulsion, there are a number of different ways to test if it will remain stable over time. Here are the most common:

1. *Viscosity vs. Time* – After the emulsion is made, measure the original viscosity and periodically thereafter to detect any large changes. If a 10% deviation from the original viscosity results in less than 3 months at room temperature, this is a sign of an unstable emulsion.
2. *Centrifuge* – Subjecting the emulsion to a 5-10 g force for several minutes will test the resistance to creaming. Although this test exerts an artificially elevated gravitational force on the emulsions, it can determine the yield strength of the emulsion that assists in maintaining stability to phase separation.
3. *Emulsion Droplet Size Analysis* – Image (microscope) or other analytical size analysis may detect a broad droplet size distribution in Pemulen o/w emulsions. Unlike conventional emulsions, this is not a predictor of emulsion instability with Pemulen resins.
4. *Heat Storage Test* – Viscosity rise of less than 20% from pre-storage samples at 50°C for one month indicates room temperature stability for one year. A viscosity rise is the precursor to visible creaming. Be sure there is as little head space as possible, as the water in the emulsion may evaporate and recondense, forming a liquid layer that may be mistakenly identified as a broken emulsion.

## Summary

Pemulen resins are universal oil-in-water emulsifiers which can provide a wide range of stable and effective emulsion forms. Traditional products can be made with unsurpassed stability, low irritancy, and improved performance, while numerous novel emulsions are limited only by the imagination.

Please contact Noveon, Inc. to discuss the product possibilities with Pemulen polymeric emulsifiers. We will be happy to provide samples, formulation assistance, pricing and other information.

For more details on specific applications for Pemulen use, please consult:

TDS-117	Skin Care Products
TDS-118	Fragrance Products
TDS-124	Cationic Skin Lotions
TDS-232-2	Waterproof Sunscreen Emulsions

Figure 9  
Effect of Mineral Oil Concentration on Pemulen TR-2 Emulsion Viscosity and Stability  
[Neutralized to pH 5.5 ± 0.2 with 18% NaOH]

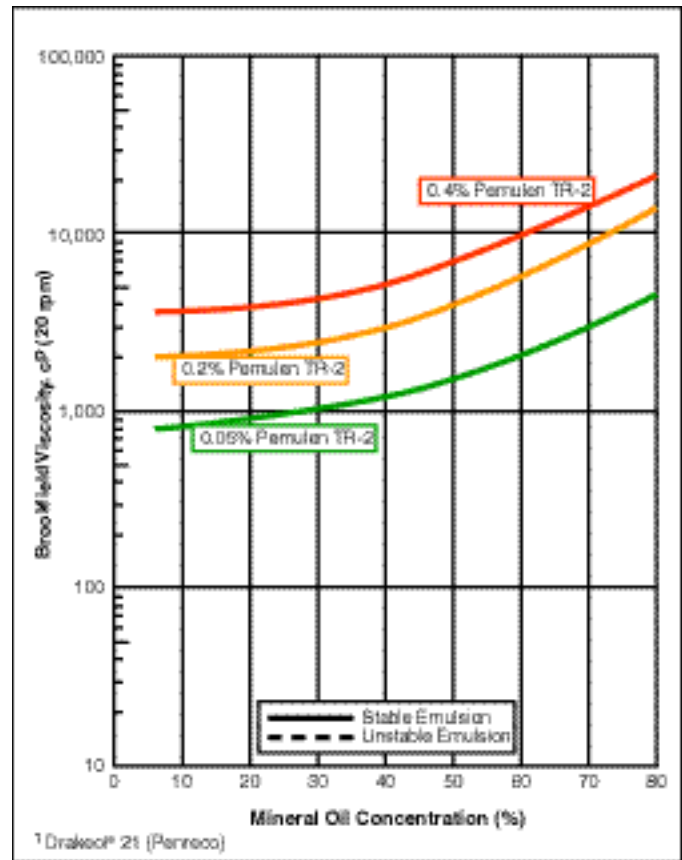
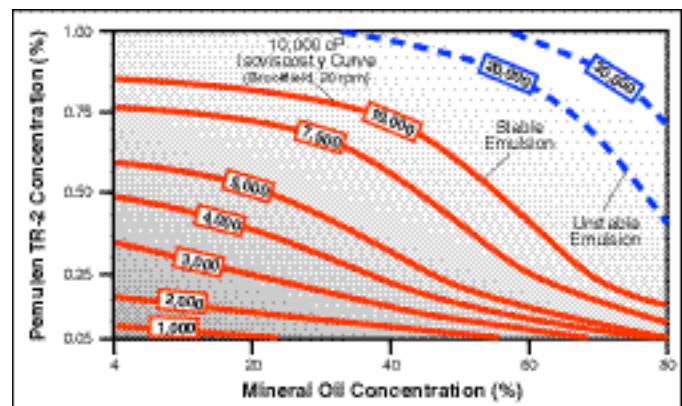


Figure 10  
Viscosity Phase Diagram for Oil/Water Emulsion  
[pH = 5.5]



## Emulsion Troubleshooting Guide

If you are having problems creating a stable emulsion, the following factors play a role in emulsion stability:

1. *pH* – The optimum pH for an emulsion using Pemulen TR-2 is 4-8. A pH above or below this range may cause an unstable emulsion.
2. *High Shear Mixing or Pumping* – Pemulen polymeric emulsifiers form a gel matrix adsorbing on the oil droplet that physically stabilizes the emulsion. High shear mixing, with colloid mills, homogenizers, etc., or high shear pumping can break down the Pemulen polymer structure resulting in viscosity loss and potentially causing emulsion creaming. If homogenization is necessary, control emulsion exposure by using an in-line homogenizer. Use low shear pumps, such as reciprocating diaphragm or auger/gear pumps.
3. *Salt or Soluble Cations* – Pemulen polymers are sensitive to salts and cations, and use of products with greater than 0.1% of strongly ionizable salts should be minimized if possible. Use deionized water. Add salts after emulsion has been formed to determine their impact.
4. *Particle Size* – Although Pemulen can produce stable emulsions with oil droplets as large as 0.5 mm in diameter, too large an oil droplet may at times make suspension of the oil droplet in water more difficult. The particle size of the oil droplet can be decreased by increasing the mixing time, using moderate shear agitation when the emulsion is made, or by use of a liquid nonionic surfactant (HLB 8-12) at 0.1-0.4 wt.%.
5. *Pemulen Level* – Modest amounts of Pemulen are used to emulsify the oil. As described earlier in this bulletin, more Pemulen is not necessarily better. As the amount of oil increases, the amount of Pemulen required to successfully emulsify it tends to be reduced. (See Figure 10)
6. *Emulsification Method Used* – If the indirect method caused an unstable emulsion, try the direct method.