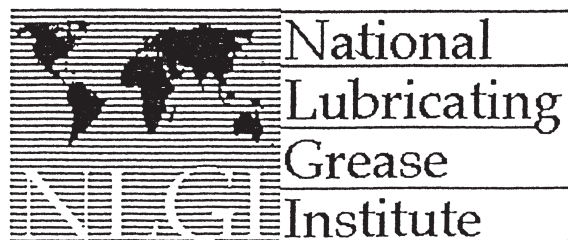


Manufacture of Polyurea Greases in A Stratco[®] Contactor[™] Reactor

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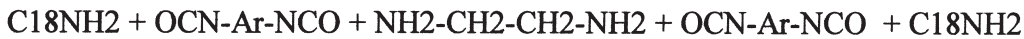
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Introduction

Polyurea greases are generally manufactured using in-line static mixers or open kettles with exceptionally good ventilation and vapor handling systems. In both procedures, exposure to starting ingredients such as fatty amines, diamines and diisocyanates (usually toluene diisocyanate) is eliminated or greatly minimized. These compounds are respiratory and skin irritants and in the case of toluene diisocyanate, somewhat toxic. The polyurea thickener described in this paper is the traditional tetraurea type made from the in-situ reaction of 2 moles of fatty amine, 2 moles of toluene diisocyanate (TDI) and 1 mole of ethylene diamine. Ideally, the reaction is driven to form a tetraurea of the type :



Where C18-NH₂ is Oleylamine

Tallowamine

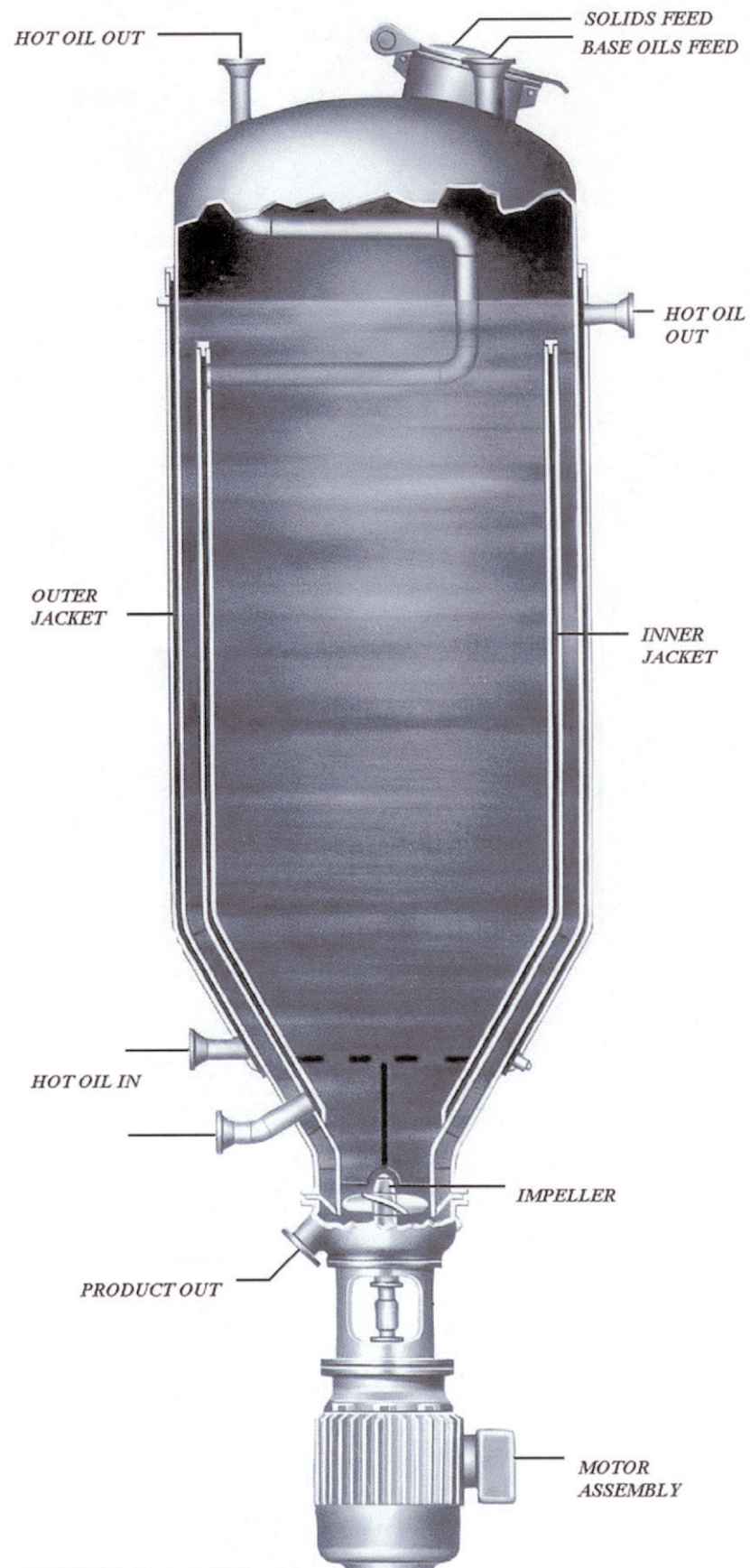
Hydrogenated tallowamine

-Ar- is 80:20 2,4 ; 2,6 – Toluy

The reaction is carried out in almost all of the oil (petroleum or synthetic hydrocarbon type) needed to form a grease. In the case of the in-line mixer, the TDI and fatty amine are dissolved in separate day tanks (kept at 120-150F) and then metered into a pipe at the correct proportions. Ethylene diamine is injected prior to the reaction mixture reaching the static mixer and in this way it is behaving as a coupling agent for the initial reaction product of TDI and fatty amine which statistically has one urea functionality and one unreacted isocyanate per molecule of TDI. Completeness of reaction is monitored by infrared (excess isocyanate exhibited at 2240 reciprocal cm) and amine titration (for excess amine).

For an open kettle operation, the amines are charged to most of the oil and warmed to about 150F prior to addition of the TDI, neat or as a solution in oil. Some operators prefer to add a solution of TDI in oil as a way of improving the texture of the final grease. Minimizing exposure to the hazardous starting components will depend on the efficiency of the ventilation system as well as the methods used to transfer starting materials from drums or totes to the reactor. Regardless of the procedure used , it usually takes about 8-12 mass % thickener to produce an NLGI 2 consistency grease.

Tetraureas prepared from petroleum oils by these procedures show the typical behavior of poor low shear stability and hardening on storage. These types represent most of the



STRATCO® Contactor™ Reactor

polyurea greases produced and are commonly used as bases for CVJ greases and sealed electric motor bearing greases.

Stratco ® Pilot Plant Studies of Polyurea Greases

In 1992, Ken Kranz and Pat Scott presented (1) successful preparations of tetraurea greases in a 12.5 gallon Stratco ® pilot reactor using formulations described in expired patents such as USP 4,661,276. In their study, the base oil was a 750 naphthenic with a VI of 46 and a pour point of -15C. For the standard non-EP tetraurea using oleylamine, ethylene diamine and TDI an NLGI 2 grade grease was obtained with 7 mass % thickener, slightly better than that claimed in the patent. In the Stratco ® pilot Contactor™ reactor, the processing time was about 1.5 hours and the top temperature used was 250F. This temperature was chosen as a study on the effect of top reaction temperature showed little change in yield between 200 and 350F, although there was a slight detrimental effect on mechanical stability and darkening for the grease prepared at 350F.

The authors also describe the successful preparation of a tetraurea grease made in technical white oil.

An EP tetraurea grease based on calcium acetate (USP 3,846,314 example 2) was also prepared efficiently in the Stratco ® pilot Contactor™ reactor.

Of particular interest was a study of neutralizing excess TDI with either ethylene diamine, water or glycerol and all were shown to be effective in eliminating the slight excess of TDI when these reactants were injected prior to reaching the top reaction temperature (250-300 F).

Production of Polyurea Greases in a Stratco ® Contactor™ Reactor

As described previously (2), a Stratco ® Contactor™ Reactor consists of a pressure vessel with an internal circulation tube, thermal fluid jackets and a hydraulic head assembly with a mixing impeller and driver. The highly turbulent circulation path results in extremely efficient mixing and heat exchange within the reactor.

A 1000 gallon Stratco ® Contactor™ Reactor, similar to the one depicted in Figure 1 is used to prepare the polyurea greases of this study. Not shown are additional venting and pressure gauge lines on top of the reactor. The tetraurea components are chosen so that approximately one drum of TDI (Net 550 lbs.) is used which will require about a drum and a half (Net 360 lbs.) of oleylamine and just a small portion of a drum of ethylene diamine to generate a grease with about 10 mass % thickener.

After charging 90-95% of the oil used in the grease formulation to the Stratco ® Contactor™ Reactor, the oleylamine and ethylene diamine are metered through a T-connection just below the pressure gauge (1" OD piping) with a small diaphragm pump. It would be possible to add these ingredients directly through the port opening. However, to minimize exposure to these components, the pumping technique is used instead. Having added the amines (and at the same time warming and circulating the reactor contents to 150-180F) the lines are flushed clean with oil and TDI is rapidly metered in with the same pump over a 10-15 minute period. Now that the TDI is in the reactor, the exothermic reaction increases the reactor contents to about 220F without heat addition by

the heating jackets. Rapid mixing is continued for about 0.5 hours and then water (1-2 gallons) is introduced to neutralize the slight excess of TDI.

The Stratco ® Contactor™ Reactor contents are then gradually heated to about 300F (0.5-1 hour) and then transferred to a finishing kettle. The reactor is rinsed with a small amount of base oil, which is then transferred to the finishing kettle. Grease in the finishing kettle is processed in the usual manner :

- Cooling to 180F
- Incorporating additives while recirculating
- Homogenization through a Manton-Gaulin homogenizer
- Penetration adjustment (to a soft NLGI 2 grade) if necessary
- Discharge to packaging

The finished grease is smooth and exhibits the rheological properties of a traditional tetraurea, i.e. softening on low-shear working and hardening on standing. For a typical tetraurea produced by this procedure, the key properties are summarized in Table 1. The Stratco ® Contactor™ Reactor prepared tetraurea grease exhibited the following characteristics :

- High Dropping Point (> 500 F)
- Smooth texture
- Excellent water resistance (water washout/spray-off)
- Low oil separation
- Load-carrying capability (through additization)

In addition, an H-1 food-grade tetraurea grease was prepared in a similar manner using a technical white oil (107.3 cSt/40C ; 11.9 cSt/ 100C ; VI – 99).

Summary

The Stratco ® Contactor™ Reactor has been demonstrated to be an effective vessel for the manufacture of polyurea greases. This procedure provides for safe handling of the urea reaction components and avoids the step of dissolving TDI in a portion of the oil, prior to reaction with the aminic components. The properties of polyurea greases prepared this way match up well with equivalent greases prepared by more conventional methods.

References

1. K. Kranz & W.P.Scott, NLGI Spokesman, 57-5, p. 19-25 (1993).
2. K. Kranz, “Grease Manufacturing in the Stratco ® Contactor Reactor “ NLGI Basic Educational Course

Table 1.

Royal Mfg. Tetraurea Grease

Typical Properties

Consistency	NLGI 2
Thickener Percent	10-12
Worked Penetration, 77F, D 217	265-295
Dropping Point, F, D 2265	525 min.
Oxidation Stability, psi drop @ 100 hrs./ 210F, D 942	5 max.
Corrosion @ 210F, D 1402	1a
Rust, D 1743	Pass
Water washout, D 1264, m% loss/179F	2.0
Water Spray-off, D 4049, m% loss/ 100F	10.0 max.
Timken OK Load, D 2509, lbs.	40 min.
4-Ball EP, D 2596, Weld Load, kgf	400
4-Ball Wear, D 2596, mm scar @ 40 kgf	0.63
Cone Oil Bleed, FTMS 791.321.3,	0.50
Base Oil Viscosity, cSt/ 100C	11.00
cSt/ 40C	144.00
Color	Aquamarine
Texture	Smooth