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DATE December 8, 1971

JOB THERMINOL CONVERSION BULLETIN

INTRODUCTION

Therminol FR(R) fire-resistant heat transfer fluids have long provided safe, dependable, economical performance for hundreds of users in dozens of applications. The presence of poly-chlorinated biphenyl (PCB) in the Therminol FR formulation provided fire-resistance, giving Therminol FR an added margin of safety which was especially desirable in hazardous applications.

Most recently, PCB has been identified as a potential hazard to the environment. Monsanto has accordingly elected to discontinue the manufacture and sale of Therminol FR fluids for heat transfer applications, and has undertaken the rather substantial task of converting Therminol FR users over to the non-PCB-containing formulations, Therminol 55 and Therminol 66.

These products offer most of the excellent heat transfer characteristics of Therminol FR fluids, and even a few additional advantages, such as a lower bulk density for improved pumpability requiring less horsepower. But in fact, Therminol 55 and 66 are not fire-resistant to the extent the Therminol FR fluids were, and due consideration must be given this fact in converting to these newer Therminol fluids.

Conversion from a Therminol FR system to a Therminol 55/66 system will be a relatively simple, low-cost procedure in the vast majority of cases. Incorporation of proper fire protection equipment will be the only consideration

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of any major consequence. But even this modification becomes academic, for with the discontinuation of Therminol FR fluids, fire protection equipment becomes necessary for any and all heat transfer media available today, since the Therminol FR fluids were unique in their fire-resistance.

This bulletin is to assist you in making the conversion to Therminol 55/66 as quickly, efficiently and economically as possible. Should questions arise, or if you run into difficulty, Monsanto's Specialty Products Group invites you to call upon its staff of qualified systems engineers for consultation at any time. Call...

(314) 694-1000

collect, and ask for a Monsanto Heat Transfer specialist.

Thank you.

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Therminol 55/66 and Your Heat Transfer System

Table I. shows the typical physical, chemical and thermal properties of Therminol FR-1 and Therminol 66. As you will note, the two products are quite similar except with regard to AIT, Fire Point and Weight per Gallon. The substantially lower weight per gallon of Therminol 66 means that pumps used in a Therminol FR-1 system will be more than adequate for a Therminol 66 system. In fact, in most cases, pumping rates will be increased with a resultant saving in horsepower requirements.

Therminol 66 has outstanding heat transfer properties, so nothing will be sacrificed from that standpoint in a change from Therminol FR-1. The specific heat and thermal conductivity of Therminol 66 are shown, along with other physical properties, in Table IV. The lower pour point of Therminol 66 ($-15^{\circ}F.$) means it will be easier to bring the system to temperature for cold startups.

Generally speaking, then, a well designed system currently operating on Therminol FR-1 can be converted to Therminol 66 with few, if any, basic changes in design -- and without sacrifice to heat transfer efficiency. With the similarity of the heat transfer properties of the two fluids thus established, let us turn to the important differences between Therminol FR-1 and Therminol 66: namely, fire-resistance and oxidation-resistance.

Fire-Resistance

As stated in the Introduction to this bulletin, the Therminol FR fluids were unique in their inherent fire-resistance. No other commonly used heat transfer medium could be so classified. Even so, the Therminol FR fluids could be made to burn under certain conditions, as indicated by their AIT of something around $1200^{\circ}F.$

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TYPICAL PHYSICAL, CHEMICAL & THERMAL PROPERTIES

	Therminol FR 1	Therminol 66	Therminol 55
Composition	Polychlorinated Biphenyl	Modified Terphenyl	Alkylated Aromatic
Maximum Bulk Temperature Rating (°F.)	600°F.	650°F.	600°F.
Recommended Use Range (°F.)	45 - 575°F.	45 - 635°F.	20 - 575°F.
Pour Point (°F)	2	-15	-40
Weight/Gallon (75°F.)	11.55	8.35	7.4
Flash Point (°F.)	350	355	355
Fire Point (°F.)	None to Boiling	374 - 392	410
AIT (°F.)	1206°F.	705	670
Boiling Range (°F.)	620 - 680	644 - 745	635 - 734
Molecular Weight	265	240	340
Expansion Coefficient cc/cc/°F.	0.00031	0.00039	0.00047

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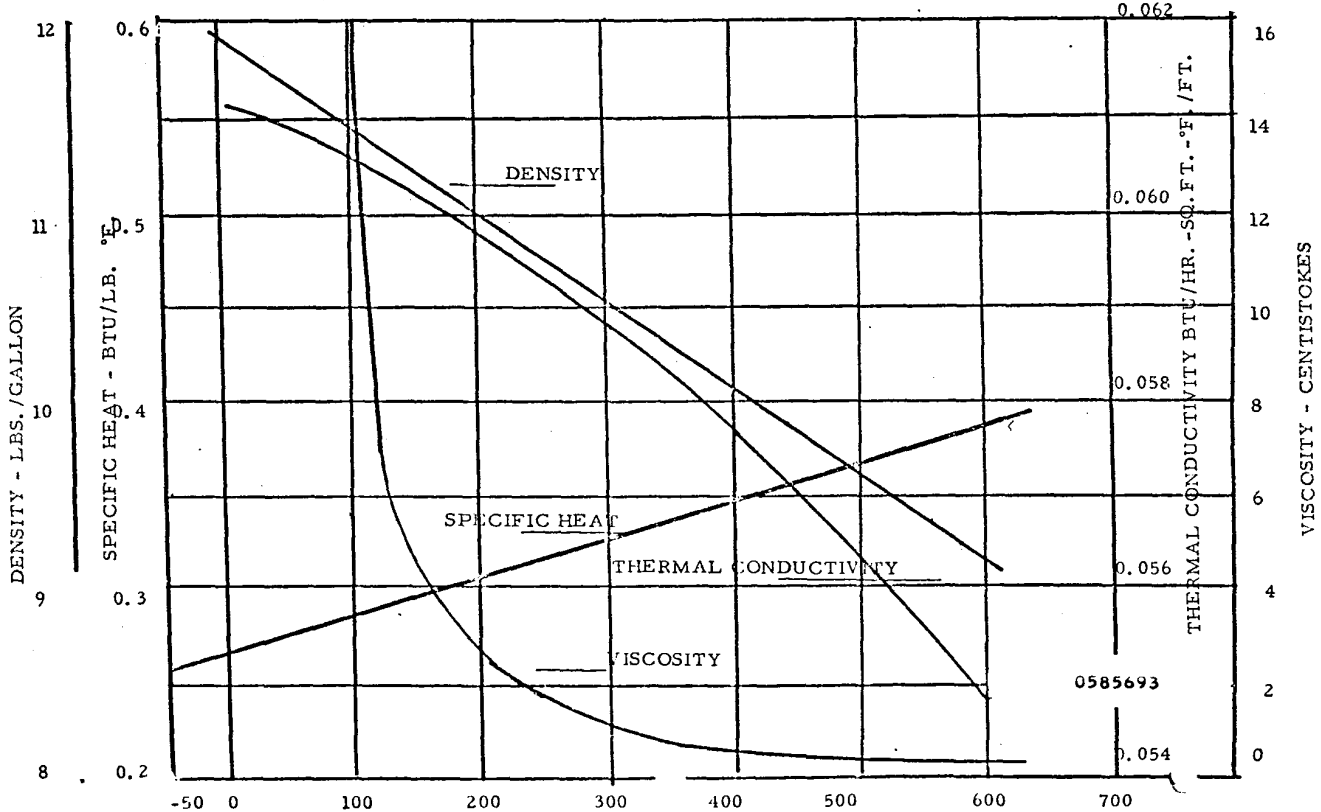
TYPICAL PHYSICAL, CHEMICAL & THERMAL PROPERTIES

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Recommended Use Range (°F.)	45 - 575°F.	45 - 635°F.
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THERMINOL® FR-1

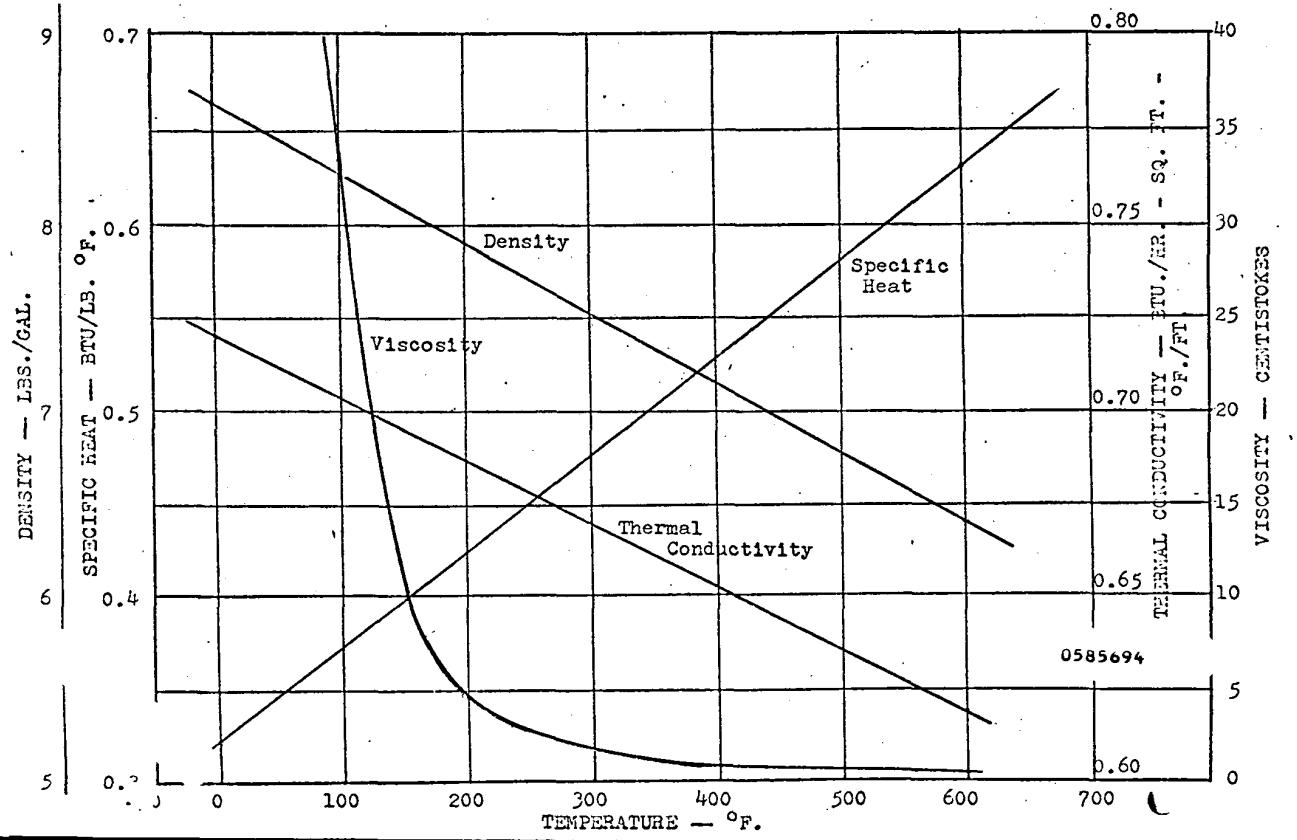
PHYSICAL PROPERTIES



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THERMINOL® 66

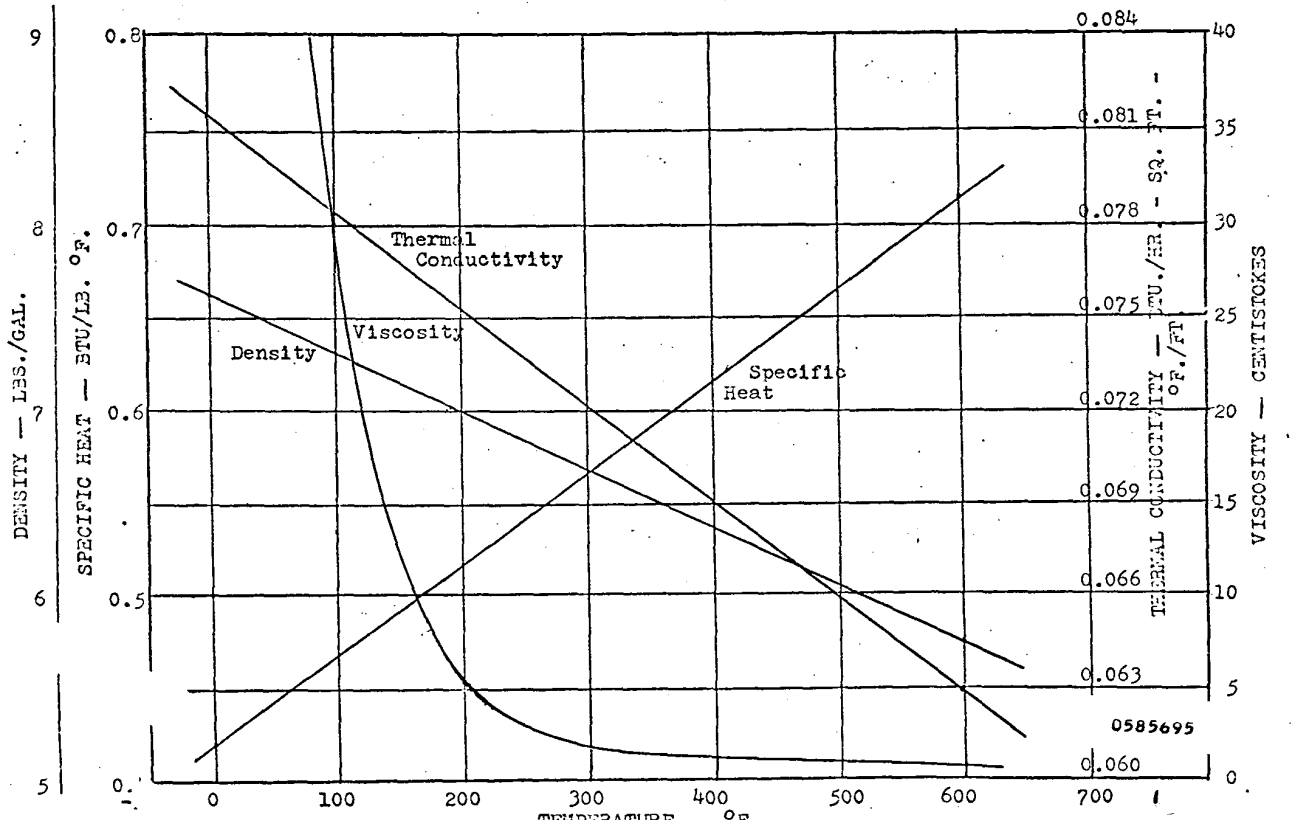
PHYSICAL PROPERTIES



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THERMINOL® 55

PHYSICAL PROPERTIES



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This point is made to emphasize that, although Therminol 66 is certainly less fire-resistant than Therminol FR-1, it should be viewed in that perspective, and not as "flammable". On a scale of fire-resistance where water would be rated as "0" and ether as "100", Therminol FR-1 would be rated "3", and Therminol 66 would fall somewhere between "15" and "20". It is important to realize that Therminol 66 is less fire-resistant than Therminol FR-1, and to modify the heat transfer system accordingly: it is equally important to understand that Therminol 66 is not a volatile, highly flammable fluid of itself.

Protecting the System

There are two major fire protection considerations in changing to Therminol 66 -- system leakage and possible tube rupture (in the heater). The former is actually part of the larger subject of good system maintenance, and should be considered regardless of the heat transfer medium employed. A tight, well-maintained system is usually a good, safe system! Following are some specific recommendations to prevent leakage when you convert to Therminol 66.

First, if your system has mechanical seals, you should enclose them, or at least provide a drip pan with a drain to a collection sump. Canned and sealless pumps offer excellent protection against leakage.

The best way to prevent piping leakage is to weld all connections. Where you must have access, use raised-face flanges with appropriate gasketing and high-temperature bolts. Controlling piping leaks is especially important, since fluid-soaked insulation poses a more serious hazard than the leaking fluid, itself.

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Organic compounds such as Therminol 66 appear to create a slow exothermal oxidation reaction with the air trapped inside the voids of the insulating material when system temperatures reach about 500°F. Saturated insulation offers a large fuel surface in the face of poor heat dissipation conditions, and this, along with possible catalysis from the insulating material (magnesia, silicate-bonded asbestos or calcium silicate) can cause a temperature build-up in the mass. This temperature build-up can far exceed the autoignition temperature of the fluid, and when the space between the piping and the saturated insulation is exposed to air (i.e., should the insulation be broken for repair, etc.), fire can result.

This phenomenon is not fully understood, but appears to occur less with closed cell insulation than with the insulating materials mentioned above. Closed cell materials, then, are preferred, especially where leakage is a possibility despite all precautions.

The principle problems areas are near thermocouple connections, valve packing glands, flanges, and wherever insulation contacts horizontal flat surfaces, such as floor plates.

To obviate this problem, eliminate any source of leakage promptly. Replace leaky gaskets, use flange back-up rings, re-pack valve stems. Cover insulation where leaks might occur with a hydraulic-setting, oil-resistant cement. Install valves, where possible, with the stems in a horizontal position so that leaks will drip away from the insulation. And again, use closed cell insulating materials on suspect piping areas.

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Tube Rupture In Fired Heaters

Generally speaking, where fire protection is concerned, it is best to consult your insurance underwriter for guidance and counsel. Likewise, you will want to discuss your fire safety equipment requirements with top-notch suppliers in that field. Selection and sizing of fire protection equipment are critical.

In the case of tube rupture in fired heaters, we recommend the piping of either steam or CO_2 as a snuffer into the combustion chamber of the heater. A minimum one-inch line with a remote manual valve for activation should a fire erupt internally is the preferred arrangement. This snuffer system can be automated by the use of an exhaust stack temperature switch. This switch would energize a solenoid valve upon excessive temperature rise, flooding the chamber with the inert snuffer automatically.

It is advisable to set the temperature switch about 100°F. over the normal exhaust temperature to prevent nuisance shutdowns. If a steam snuffer system is used, it is a good idea to employ a steam trap to avoid slugging the combustion chamber with water when the system activates, or is activated manually.

You can obtain a basic guideline in the selection of CO_2 protection equipment (again, it is best to consult your insurance underwriter) from the National Fire Protection Assn.,

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Booklet Number 12, dated 1968. In this publication, it is stated that a minimum CO_2 concentration of 46% in the combustion chamber will extinguish a Therminol fire. The following table will be useful in determining the volume of CO_2 required:

Volume of Combustion Chamber - Cubic Feet	Calculated Quantity* CO_2 Pounds	Temp. Corrected** CO_2 Pounds
0 - 140	15	30
141 - 500	15	30
501 - 1600	53	106
1601 - 4500	150	300

* Calculated quantity of CO_2 required to maintain 46% concentration by volume at temperatures of 200°F. or less.

** Temperature corrected quantity of CO_2 required to maintain 46% concentration by volume at temperatures of 700°F. (Rule of thumb: increase volume of CO_2 by 1% for every additional 5°F. over 200°F.)

CO_2 cylinders are available from Cardox Division of Chemetron, Chicago, Illinois. Standard sizes available and approximate costs are as follows:

CO_2 Pounds Cylinder Size	Single Automatic	Double Automatic
50	$410	$610
75	$460	$710
100	$650	$980

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These units and prices include drawings of the units, fully-

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charged cylinders, flexible piping connectors, spray nozzle, pressure switch, alarm and automatic control, provided CO_2 release signal is supplied by customer device. Piping, wiring and installation labor is provided by the customer. Recharging of cylinders is available at a cost of $15.00 to $25.00 from a variety of "Fire & Safety Equipment Suppliers" listed in the Yellow Pages of your phone book.

In the normal installation a single cylinder would be released to extinguish the fire, with a second unit available as standby. The second cylinder could actually be used for extended discharge to maintain maximum concentrations, since some CO_2 will obviously be lost by leakage from the combustion chamber. This arrangement could prevent re-ignition while the heater is cooling.

The Halone Fire Suppression System is a possible alternative to a CO_2 arrangement, and can be used in closed spaces with personnel in the area. Far less concentration is required than with the CO_2 system, but the Halone system is more costly to recharge, facilities to do so are not as readily available, and the latter system is a "fire suppression" arrangement as opposed to a "fire extinguishing" system.

Again, we strongly recommend that the advice of fire protection companies be solicited in either case to insure proper equipment selection and installation.

Table ____ shows the amounts of snuffing steam required in the combustion chamber for control, if steam is to be used rather than the other alternatives suggested above.

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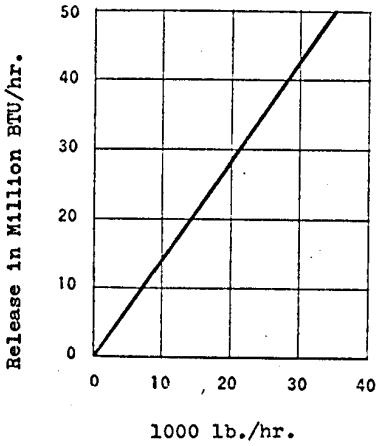


Figure ____ -- Rate of Steam Introduction in 1000 lb./hr.

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Oxidation-Resistance

With a Therminol 66 system, some provision should be made to prevent oxidation caused by air contact at fluid temperatures exceeding 200°F. This was not the case with Therminol FR fluids, but must be observed for the newer-generation fluids. Oxidation can result in sludge formation, eventually leading to loose carbonaceous deposits on heat transfer surfaces.

Oxidation is normally the product of an open, vented expansion tank, and we therefore recommend that the expansion tank be blanketed with an inert gas. If this is not possible, use a cold seal arrangement as shown in Table ____. An inert gas pressure of one to two psi should be adequate, as Therminol 66 does not require presurization.

You can design the cold seal arrangement quite simply by piping the expansion tank vent to a second tank where the vent line can be flooded with additional Therminol 66 to prevent air contact in the vapor space.

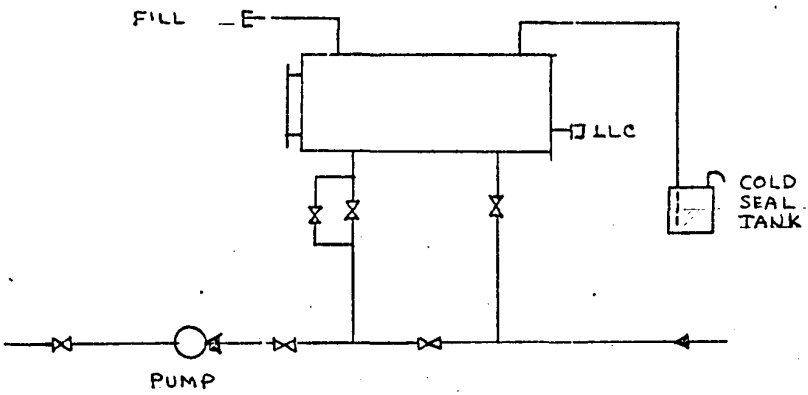
In converting from Therminol FR to Therminol 66, it is important to remember that many Therminol FR systems were designed with a hot bleed line into the expansion tank to eliminate moisture accumulation. This bleed line should be eliminated in a Therminol 66 system.

Carbonaceous deposits can also occur at the pump seal face due to leakage at high temperatures. The use of a sealguard flush system or a double mechanical seal is helpful in preventing this.

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SUGGESTED
EXPANSION TANK LAYOUT

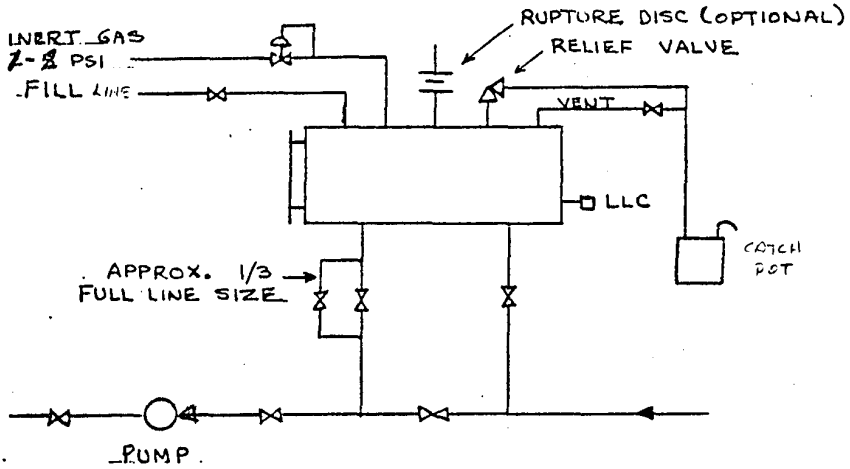
COLD SEAL LAYOUT



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INERT GAS BLANKETED LAYOUT



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CONVERTING TO THERMINOL 66

With fire-protection and oxidation-resistance procedures well in mind, let us turn to the matter of preparing the Therminol FR system to accept Therminol 66.

The most expedient procedure would be to simply drain and change the system to Therminol 66: however, expedience is not always the best alternative, and certainly not in this case.

Debris accumulated over the years in the system could cause serious problems, especially to mechanical seals, rotary joints, etc. (see Suggested Expansion Tank Layout, Table _____). Any heat transfer system should be drained and cleaned from time to time as a part of normal preventive maintenance. Since a fluid change is necessary at this time, it would seem logical to use the downtime to clean up the system and start fresh. We would strongly advise you not to simply drain and change, but to take this opportunity to clean your system. Many potential problems will be preempted by so doing.

The other reason for cleaning your system at this time is that the system should be completely purged of PCBs, and a system cleanout is the only sure way to do so. How to go about the cleanout is a matter of choice, but here are some alternatives for your consideration:

A. CHEMICAL CLEANING

This method is particularly effective in cleaning heavily-fouled heating surfaces.

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Cleaning service may be purchased from Dow Industrial Service Company or Halliburton...or, it may be done in-house using Oakite cleaning products or caustic soda and soda ash. Consult the Yellow Pages of your phone book for the above services and suppliers.

Chemical cleaning procedure with caustic soda and soda ash follows: contact Oakite for detailed information on their procedure.

Chemical Cleaning - Caustic Soda and Soda Ash

1. Fill empty system with cleaning solution containing 5 lb. caustic soda and 5 lb. soda ash per 120 gallons of water.
2. Initiate circulation* and heat liquid to 180°F.
3. Circulate 24 hours, periodically drain fluid from a low point and replace with clean water. Do this until fluid in system is clear (about 24 hours).
4. When fluid in system is clear, raise temperature to 215°-225°F, stop pump and heater.
5. Quickly drain system, open all vents, and allow residual heat to dry system.
6. Assure system is dry.
7. Fill with Therminol ~~fluid selected.~~ 66.

*May be desirable to pack pump with Teflon filled asbestos packing to prevent damage to mechanical seal faces.

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B. FLUID FLUSH CLEANING

This system is probably the fastest and most effective where heating surfaces are not heavily fouled. It also offers the advantage of not having to introduce foreign chemicals into the system.

With this method, the system is drained of Therminol FR, re-filled with Therminol 66, (Therminol 55 may also be used), operated for a reasonable period of time, drained once again, and finally, re-charged with fresh Therminol 66.

Both the drained Therminol FR and the Therminol 55/66 used to flush the system may then be returned to Monsanto for disposal at no cost to you, assuring you of a PCB-free system, and a fresh start.

C. SOLVENT CLEANING

This method is satisfactory for cleaning a slightly soiled system, but chlorinated solvents must be avoided. Typical solvents used are acetone, benzene, kerosene and xylol. Do not use trichlorobenzene or perchloroehtylene. (CAUTION: ALL SOLVENTS SHOULD BE COMPLETELY REMOVED FROM THE SYSTEM PRIOR TO CHARGING WITH THERMINOL 66).

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Fluid Disposal

All drained Therminol FR and Therminol 55/66 flushing fluid should be returned to Monsanto for incineration. This service is provided at no cost to you, and assures proper elimination of PCBs from the environment.

All such material should be shipped to:

Monsanto Company
W. G. Krummrich Plant
Sauget, Illinois
ATTN: Supervisor, Dept. 246

Please make certain that shipped materials are properly identified.

As stated earlier, Monsanto maintains a staff of qualified engineers who will be available for consultation should you have questions or run into difficulties. The number to call, again, is (314)694-1000: ask for a Monsanto Heat Transfer Specialist.

Thank you.

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