T E C H N I C A L B U L L E T I N

THERMINOL® CONVERSION BULLETIN

SP/TC-1

Monsanto

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Monsanto Industrial Chemicals Co.
A Unit of Monsanto Company
800 N. Lindbergh Blvd., St. Louis, Mo. 63166

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INTRODUCTION

Therminol FR® 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. This bulletin is to inform you about two alternative products sold by Monsanto which do not contain PCB, namely 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 specific gravity for improved pumpability requiring less horsepower. We would point out that 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. You may wish to consult with your insurers on any conversion from Therminol FR.

Conversion from a Therminol FR fluid to a Therminol 55 or 66 fluid will be a relatively simple, low-cost procedure in the majority of cases. Incorporation of proper fire protection equipment will be the only consideration of major consequence in most cases. But even this modification becomes academic, for with the discontinuation of Therminol FR fluids, fire protection equipment becomes necessary for any and all low pressure heat transfer media available today, since the Therminol FR fluids were unique in their fire-resistance.

Should questions arise with respect to the conversion from Therminol FR fluid, Monsanto's Specialty Products Group invites you to call upon its staff or qualified systems engineers for consultation at any time. Call . . .

(314) 694-2514

and ask for a Monsanto Heat Transfer Specialist.

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Therminol 55 and 66 and Your Heat Transfer System

Table 1 shows the typical physical, chemical and thermal properties of Therminol FR-1, Therminol 55 and Therminol 66. As you will note, Therminol 55 and 66 are quite similar except with regard to AIT, Fire Point and density. The substantially lower density of Therminol 55 and 66 means that pumps used in a Therminol FR-1 system should be adequate for a Therminol 55 and 66 system. In most cases, pumping rates will be increased with a resultant saving in horsepower requirements.

TABLE 1

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
Pounds/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

Therminol 55 and 66 have outstanding heat transfer properties, so heating and cooling performance will not be sacrificed in a change from Therminol FR-1. The specific heat and thermal conductivity of Therminol 55 and 66 are shown, along with other physical properties, in Tables 2, 3 and 4, and in Figures 1, 2 and 3. The lower pour points of Therminol 55 and 66 will provide easier cold startup of the system.

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TABLE 2

THERMINOL® FR-1
VARIATION OF PROPERTIES WITH TEMPERATURE

Temperature		Density		Specific Heat		Thermal Conductivity		Viscosity		Vapor Pressure	
°F	°C	lb/gal	Kg/m³	BTU/lb °F	Kcal/Kg °C	BTU/ft hr °F	Kcal/m hr °C	Cp	Cs	mmHg absolute	Kg/cm²
50	10	11.68	1399.6	0.272	0.272	0.06098	0.0907	308	220	—	—
100	38	11.46	1372.7	0.282	0.282	0.06060	0.0902	23.2	16.9	—	—
150	66	11.22	1343.7	0.291	0.291	0.06021	0.0896	6.6	4.9	—	—
200	93	10.99	1316.7	0.3047	0.3047	0.05976	0.0889	3.4	2.6	—	—
250	121	10.76	1289.1	0.3151	0.3151	0.05927	0.0882	2.3	1.8	—	—
300	149	10.53	1261.3	0.3255	0.3255	0.05875	0.0874	1.4	1.1	—	—
350	177	10.30	1233.5	0.3359	0.3359	0.05819	0.0866	1.0	0.8	10	0.0136
400	204	10.07	1205.8	0.3464	0.3464	0.05760	0.0857	0.8	0.7	27	0.0367
450	232	9.83	1178.0	0.3568	0.3568	0.05697	0.0848	0.6	0.5	65	0.0884
500	260	9.60	1150.2	0.3672	0.3672	0.05630	0.0838	0.5	0.4	143	0.1945
550	288	9.37	1122.5	0.3776	0.3776	0.05560	0.0827	0.4	0.4	291	0.3958
600	316	9.14	1094.7	0.3880	0.3880	0.05487	0.0817	0.4	0.3	550	0.7480
650	343	8.91	1066.9	0.3985	0.3985	0.05409	0.0805	0.3	0.3	18.8psia	1.3218
700	371	8.68	1039.3	0.4089	0.4089	0.05329	0.0793	0.3	0.3	31.9psia	2.2429

TABLE 3

THERMINOL® 66
VARIATION OF PROPERTIES WITH TEMPERATURE

Temperature		Density		Specific Heat		Thermal Conductivity		Viscosity		Vapor Pressure	
°F	°C	lb/gal	Kg/m³	BTU/lb °F	Kcal/Kg °C	BTU/ft hr °F	Kcal/m hr °C	Cp	Cs	mmHg absolute	Kg/cm²
0		8.67	1040	0.320	0.320	0.0720	0.1072	62000	50000	—	—
50	10	8.51	1020	0.350	0.350	0.0711	0.1058	255	250	—	—
100	38	8.34	1000	0.380	0.380	0.0703	0.1046	28.0	28.0	—	—
150	66	8.14	975	0.405	0.405	0.0695	0.1034	9.75	10.0	—	—
200	93	7.91	950	0.430	0.430	0.0687	0.1022	4.18	4.40	0.1	—
250	121	7.77	930	0.455	0.455	0.0678	0.1008	2.42	2.60	—	—
300	149	7.59	910	0.480	0.480	0.0670	0.0997	1.55	1.70	2.0	0.003
350	177	7.39	885	0.505	0.505	0.0662	0.0985	1.06	1.20	—	—
400	204	7.17	860	0.530	0.530	0.0653	0.0972	0.77	0.90	20.0	0.027
450	232	7.04	840	0.555	0.555	0.0645	0.0959	0.58	0.69	50.0	0.068
500	260	6.75	810	0.580	0.580	0.0637	0.0948	0.45	0.55	100.0	0.136
550	288	6.62	793	0.605	0.605	0.0628	0.0935	0.36	0.46	200.0	0.272
600	316	6.42	770	0.630	0.630	0.0620	0.0923	0.34	0.44	350.0	0.476
650	343	6.24	750	0.655	0.655	0.0613	0.0912	0.27	0.36	760.0	1.034
700	371	6.09	730	0.680	0.680	0.0605	0.0900	0.20	0.28	1000	1.360

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TABLE 4

THERMINOL® 66
VARIATION OF PROPERTIES WITH TEMPERATURE

Temperature		Density		Specific Heat		Thermal Conductivity		Viscosity		Vapor Pressure	
°F	°C	lb/gal	Kg/m³	BTU/lb °F	Kcal/Kg °C	BTU/ft hr °F	Kcal/m hr °C	Cp	Cs	mmHg absolute	Kg/cm²
0	—18	7.62	915	0.420	0.420	0.0813	0.1210	1472	1610	—	—
100	38	7.31	878	0.472	0.472	0.0784	0.1167	25.4	30.1	0.5	0.001
200	93	7.00	840	0.522	0.522	0.0753	0.1121	4.20	5.0	3.0	0.004
300	149	6.69	803	0.572	0.572	0.0724	0.1077	1.69	2.10	10	0.014
400	204	6.39	766	0.620	0.620	0.0692	0.1030	0.904	1.18	40	0.054
500	260	6.07	729	0.670	0.670	0.0661	0.0984	0.583	0.80	100	0.136
600	316	5.76	691	0.718	0.718	0.0630	0.0938	0.415	0.60	250	0.330

FIGURE 1
THERMINOL® FR-1
PHYSICAL PROPERTIES

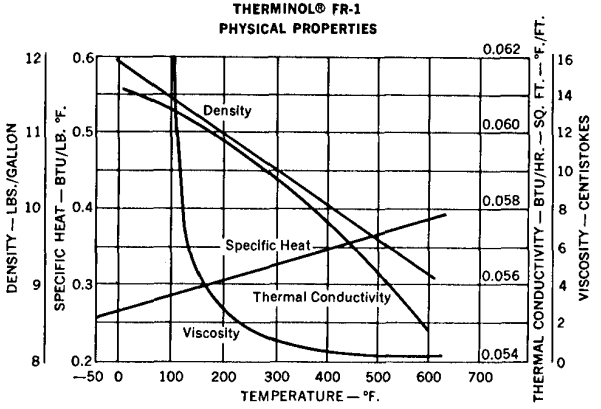

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FIGURE 2
THERMINOL® 66
PHYSICAL PROPERTIES

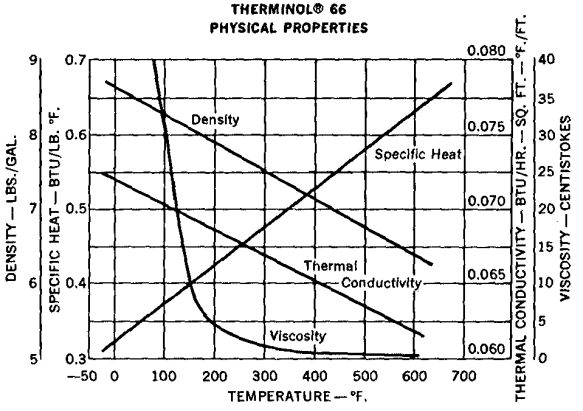
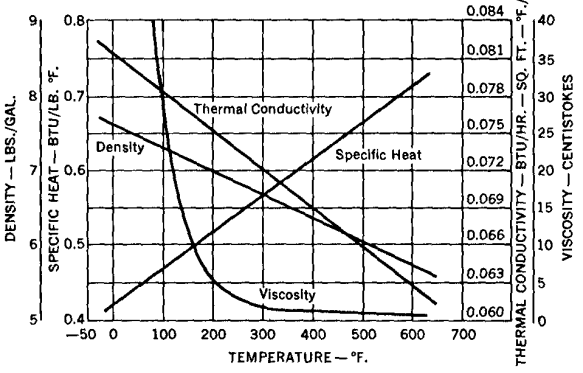


FIGURE 3
THERMINOL® 55
PHYSICAL PROPERTIES



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Generally speaking, then, a well designed system currently operating on Therminol FR-1 can be converted to Therminol 55 and 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 three fluids thus established, let us turn to the important differences between Therminol FR-1 and Therminol 55 and 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 about 1200°F.

It is important to realize that Therminol 55 and 66 are less fire-resistant than Therminol FR-1, and to modify the heat transfer system accordingly; it is equally important to understand that Therminol 55 and 66 are *not* volatile, highly flammable fluids, but rather combustible as defined by FM and NFPA (*NFPA No. 321*).

Protecting the System

There are two major fire protection considerations in changing to Therminol 55 or 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 suggestions to prevent leakage when you convert to Therminol 55 or 66.

First, if your system has rotary mechanical seals, you should provide a spray shield and a drip pan with a drain to a collection sump. Canned and seal-less 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 bolting. Control of piping leaks is especially important, since fluid-soaked insulation poses a more serious hazard than the leaking fluid, itself.

Organic compounds such as Therminol 55 and 66 exhibit a slow 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 result in ignition of the fluid when the space between the piping and the saturated insulation is exposed to air (i.e., should the insulation be broken for repair, etc.).

This phenomenon is not fully understood, but appears to occur less with closed cell insulation than with the insulating materials mentioned

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above. Closed cell materials, then, are preferred, especially where leakage is a possibility despite all precautions.

The principle problem areas are near instrument connections, valve packing glands, flanges, and where cracks develop in relatively impermeable insulation cement adjacent to oil soaked insulation.

To obviate this problem, eliminate any source of leakage promptly. Replace leaky gaskets, oil soaked insulation, and 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.

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 qualified suppliers of fire protection equipment. Selection and sizing of fire protection equipment is important to safeguard the installation.

A commonly used method of preventing fire in the event of tube rupture in fired heaters is piping steam or CO_2 as a snuffer into the combustion chamber of the heater. Usually a properly-sized line with a *remote* manual valve for activation is the preferred arrangement. This snuffer system could be automated by the use of an exhaust stack temperature switch. This switch would then energize a solenoid valve and alarm upon excessive temperature rise, automatically flooding the chamber with a fire extinguishing agent.

In practice the temperature switch is often set about 100°F. *over* the normal exhaust temperature to prevent nuisance shutdowns. Where steam snuffer systems are 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., 60 Batterymarch Street, Boston, Mass. 02110 AC 617-482-8755. NFPA Bulletin No. 12 dated 1968 should be requested. This bulletin should be helpful in determining the amount of CO_2 and the concentration of CO_2 needed to extinguish a fire based on your specific application.

CO_2 cylinders are available from Cardox Division of Chemetron, Chicago, Ill. as well as other suppliers. Some standard sizes are 50, 75, 100 and 150 pound cylinders. Prices usually include drawings of the units, fully 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 to be provided by the customer. Recharging of spent cylinders is available at an additional cost from a variety of "Fire & Safety Equipment Suppliers" listed in the Yellow Pages of your phone book.

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Selection of all equipment and installation recommendations should be obtained from qualified suppliers; however, it is important to insure that sufficient CO_2 is available to prevent re-ignition while the heater is cooling.

The Halon Fire Suppression System is a possible alternative to a CO_2 arrangement because it can be used in closed spaces with personnel in the area. One supplier of Halon systems is the Cardox Division of Chemetron Corporation, Chicago, Ill. 60611.

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

If steam is to be used rather than the other alternatives suggested above, please refer to the NFPA Volume I, Section 86A (1970-1971) to obtain the volume of steam required.

Oxidation-Resistance

With a Therminol 55 or 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 Therminol 55 and Therminol 66. Oxidation can result in sludge formation, eventually leading to carbonaceous deposits on heat transfer surfaces and at mechanical seal faces.

Oxidation of fluid can develop by air contact in an open, vented expansion tank. Therefore, we recommended that the expansion tank be blanketed with an inert gas (such as nitrogen) as shown in Figure 4. If this is not possible, air contact can be minimized by a cold seal arrangement as shown in Figure 5. An inert gas pressure of one to two psi is adequate, as Therminol 55 and 66 do not require pressurization to maintain liquid phase.

FIGURE 4
SUGGESTED INERT GAS ARRANGEMENT
FOR EXPANSION TANK

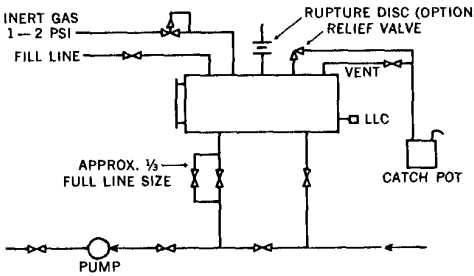

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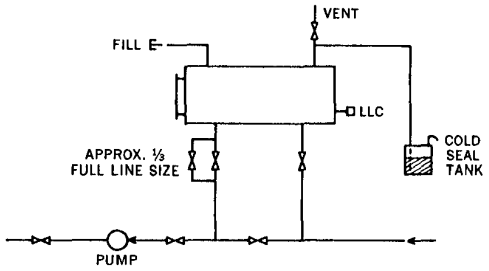
FIGURE 5
SUGGESTED COLD SEAL TRAP ARRANGEMENT FOR EXPANSION TANK



You can design the cold seal arrangement quite simply by piping the expansion tank vent to a second tank where the vent line projects subsurface and can be flooded with additional Therminol 55 or 66 to minimize air contact in the expansion tank vapor space.

In converting from Therminol FR to Therminol 55 or 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. Moisture accumulation in the presence of hydrogen chloride gas released during the decomposition of the FR fluids could contribute to acidity problems. This is not the case with Therminol 55 or 66; *therefore, this bleed line should not be used during normal operation of a Therminol 55 or 66 system.* This line should be *valved off* during operation but it could be retained as a convenient means of venting the system during initial startup after conversion.

Further protection against a hot expansion tank occurrence would be the removal of any expansion tank insulation and feeder line insulation.

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

Converting to Therminol 55 and 66

With fire-protection and oxidation-resistance procedures well in mind, let us turn to the matter of preparing the Therminol FR system for Therminol 55 or 66.

Accumulation of debris over the years in the system could cause serious problems, especially to mechanical seals, rotary joints, etc. All heat transfer systems should be cleaned from time to time as a part of normal preventive maintenance. Since a fluid change is neces-

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sary at this time, it would seem practical to use the downtime to thoroughly clean the system prior to startup on a fresh charge of fluid.

We strongly advise you *not* to simply drain and change, but to take this opportunity to clean your system. Many potential problems will be prevented by so doing.

Another reason for cleaning your system at this time is to assure complete removal of the Therminol FR fluid. 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. *Fluid Flush Cleaning*
This method 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 55 or 66, operated for a reasonable period of time, drained once again, and finally, recharged with fresh Therminol 55 or 66.

Both the drained Therminol FR and the Therminol 55 or 66 used to flush the system may then be returned to Monsanto for disposal.

B. *Solvent Cleaning*
This method is satisfactory for cleaning a slightly soiled system, but chlorinated solvents must be avoided. Typical solvents used are benzene, and xylol (caution should be used with low flash point solvents). Do not use trichlorobenzene or perchloroethylene. (CAUTION: ALL SOLVENTS SHOULD BE *COMPLETELY* REMOVED FROM THE SYSTEM PRIOR TO OPERATING AT HIGH TEMPERATURES). Normally this is accomplished by drying the residual with warm air or by operating the refilled Therminol system at a temperature slightly above the boiling point of the solvent until the residual is vented from the system. Some *caution* should be used in drying the system to prevent flashing of the solvent with resultant discharge of Therminol from the system. Both the drained Therminol FR and the flushing solvent may then be returned to Monsanto for disposal.

Fluid Disposal

Monsanto offers an incineration service for the disposal of PCB heat transfer fluids and the flushing fluids mentioned above. For details of this service and how to return fluids to Monsanto for disposal, please write:

Monsanto Company
P.O. Box 14617
St. Louis, Missouri 63178

. . . or call (314) 694-2514 and ask for a Monsanto Heat Transfer Specialist.

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Handling: General Information

Heat transfer fluids are intended only for indirect heating purposes. Under no circumstances should any Therminol heat transfer fluid be allowed to come in contact with or in any way contaminate food, animal feed, food products, food packaging materials, food handling equipment, pharmaceuticals or *any* food-related items.

Therminol 55 and Therminol 66: Safety of Handling

According to the definitions of the U.S. Federal Hazardous Substances Labeling Act, Therminol 55 and 66 are not toxic substances since the oral and dermal lethal doses in animals are greater than 5 grams per kilogram of body weight. Additional animal studies indicate that they do not have significant skin or eye irritation potential. It is suggested however, that good industrial practice relating to the avoidance of repeated and prolonged skin contact to any industrial chemical, heat transfer fluids, or petroleum product be followed.

Therminol 55 and 66 have such low vapor pressures at ambient temperature that inhalation of vapors during transfer of fluid from shipping containers to a heat transfer system presents no hazard. Vapors emitted by either fluid at elevated temperatures may be irritating as would be the case with excessively heated petroleum oils. In heat transfer installations, the fluids are used in a closed, unpressurized system free from leaks and with the expansion tank vent trapped so as to condense any vapors and thus prevent their escape to the work environment. Consequently, there should be little or no opportunity for workers to experience any contact or exposure.

While it is believed that Therminol 55 and 66 pose no serious problems with respect to the environment, as a concerned supplier to industry, Monsanto urges the user to maintain a tight system, to correct leakage promptly, and to exercise care in the handling and disposal of this and all other such products. A tight maintenance program not only protects the environment, but keeps employes comfortable, the working area clean, and the system running smoothly.

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