綜 說

Intermediates for the Production of Polyurethanes

*Peter H. Spitz

Flexible and rigid polyurethane foams and other urethane products, such as coatings, elastomers, fibers, and adhesives have exhibited high growth rates in major world markets and will continue to grow very rapidly over the next 10—15 years. In the United States, for example, flexible and rigid urethane foams are expected to grow at a compound annual rate of 12 and 15 %, respectively, through 1980. While the West Eurapean and U. S. annual growth rate for urethane foams for the 1964-71 period was over 15%, that for Japan was higher. In terms of production volumes, the numbers are equally impressive. In Japan, for example, only 53,000 metric tons of polyurethane foam were produced in 1968, but this output should increase to a level of 300,000 metric tons by 1980.

The dramatic growth in the consumption of foamed plastics generally, and polyurethane foams in particular, has been due to a combination of declining raw material prices and rapidly broadening consumption patterns during a period of the successful promotion of applications knowhow. While flexible foams have penetrated traditional home furnishing bedding and upholstery markets, the rigid foams have found increased acceptance in structural applications in construction, furniture and transportation areas. A detailed breakdown of the polyurethane foam market in the United States is outlined in Table 1. Table 2 summarizes the composition of the Japanese urethane foam market and the utilization of flexible and rigid foams in the major countries of Western Europe is indicated in Figures 1 and 2.

* Carl A. Steinbaum Chem. Systems, Inc.

Table 1. United States Market for Polyurethane Foams (MM pounds of foam product)

	1968	1969	1970	1971	1975*	1980*
Flexible Foams:						
Furniture	170	245	240	260	400	600
Transportation	150	175	195	200	450	700
Bedding	50	58	75	83	150	210
Other	85	98	143	160	300	520
Total Flexible	455	576	653	703	1300	2030
Rigid Foams:						
Appliances	50	55	62	65	80	120
Construction	36	63	83	95	210	450
Transportation	30	38	45	50	80	140
Furniture	10	25	28	35	90	210
Other	33	28	34	35	50	80
Total Rigid	157	209	252	280	510	1000
TOTAL FOAMS	612	785	905	983	1810	3030

*Chem Systems' Estimate

Table 2. Polyurethane Foam Market in Japan (% of Total Consumption)

Flexible Foam	
Bedding	22
Transportation	26
Furniture	13
Apparel	6
Others	14
Total Flexible Foam	81
Rigid Foam	
Appliances & Other Equipment	8
Construction	6
Transportation	3
Miscellaneous	2
Total Rigid Foam	19
TOTAL FOAMS	100

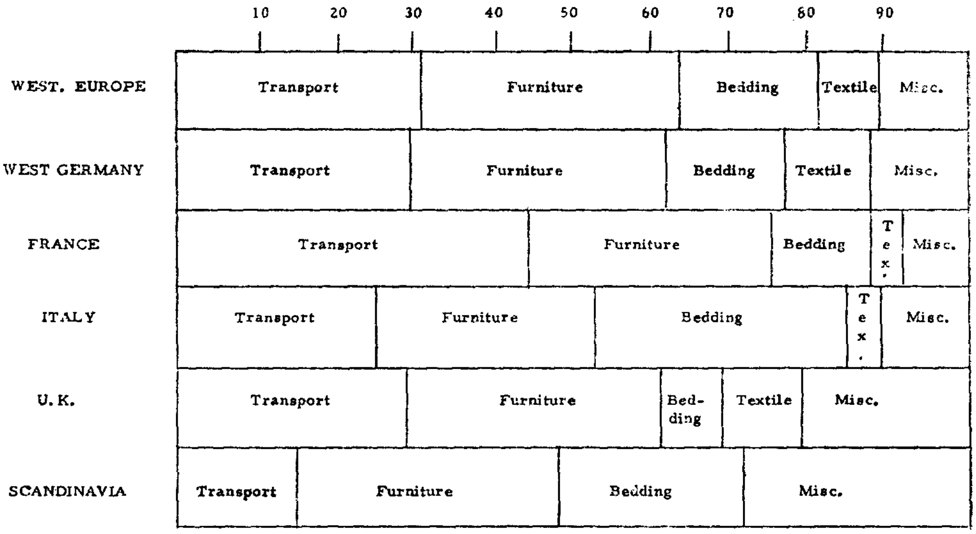


Fig. 1. Breakdown of Flexible Urethane Foam Consumption by End Use, 1971 (percentage)

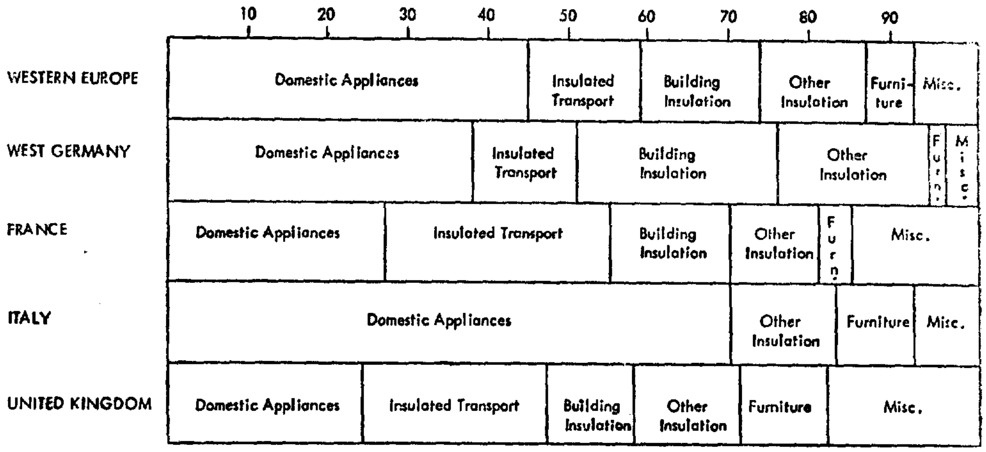


Fig. 2. Breakdown of Rigid Urethane Foam Consumption by End Use, 1971 (percentage)

In the United States and Western Europe urethane products dominate the foamed plastics area. Although the continuing development and promotion of polyethylene, polystyrene and polyvinyl chloride cellular materials will undercut this position during the seventies, urethane products will still account for over 50% of the foamed product areas by 1980.

On the basis of the above, polyurethane products and their intermediates-the isocyanates and polyols—will be among the most rapidly growing petrochemicals during this decade and beyond. For this reason, countries building an advanced petrochemical industry should examine the possibility of either the production of polyurethanes or the intermediates used in their manufacture.

While such an analysis may result in a decision to delay the commercialization of a facility to produce isocyanates and/or polyols, there is no doubt that the polyurethane industry has reached a point where it must be evaluated at the same stage of industrial development as that of several of the other major plastic intermediates and end-products.

A. Flexible and Semi-rigid Urethane Foams

These materials are produced by the reaction of a diisocyanate with relatively high molecular weight polyfunctional hydroxyl compounds, known as polyols or polyethers. The principal isocyanate used in flexible foam manufacture is tolylene diisocyanate (TDI). The commercial material is generally an 80/20 mixture of the 2, 4 and 2, 6 isomers. Mixtures of TDI and polymethylene polyphenyl isocyanate (PMPPI) are used for the production of high resilience foams. The polyols are principally propylene oxide adducts of such polyalcohols as glycerin and trimethylol propane (TMP) or 1, 2, 6 hexanetriol. Increased use of ethylene oxide in the polyether polyol structure has broadened the utilization of the flexible urethane foam. The ethylene oxide can be added by either random or blocked methods. By modifying the polyol structure or using polyol mixes in combination with specific isocyanates, foam producers can "tailor" the product to fit the desired application. Examples of flexible foam applications include furniture cushions, armrests and headrests, mattresses and pillows, automobile seat cushioning sun visors and door insulation, carpet underlays and gasketing. The markets for semi-rigid foams include automobile dash board panels and armrests, aircraft interiors and cockpit cushioning, door mats, roof insulation and packaging.

TDI is by far the most important isocyanate utilized for production of flexible and semi-rigid urethane foams.

B. Rigid Urethane Foams

Rigid urethanes are produced by the reaction of low molecular weight propylene oxide adducts of polyalcohols or polyamines such as sorbitol, α-methyl glucoside and ethylenediamine with different isocyanates or isocyanate mixtures. The principal isocyanates which are used include polymeric isocyanates and an undistilled grade of mixed TDI isomers. The latter has a TDI content of 85%, with the remainder being various phosgenated by-products, while the former is derived from an aniline-for maldehyde condensation product and is in essence an isomer mixture.

The main market for these materials are the construction, household, transportation and furniture industries, where rigid foams are used for insulation (e. g. house and mobile home construction, refrigerators, refrigerated trucks), panel cores and structural members. In construction and furniture applications, the polymeric isocyanates, largely PMPPI, dominate the field, while TDI-based foams account for much of the household and refrigeration markets.

The development of so-called self skinning furniture systems has yielded a product that is gaining consumer appeal and competes directly with wood for the production of both custom and mass-produced furniture. At present, substantial efforts are being directed at improving urethane flame retardancy. As these improvements occur and local building codes are modified, the use of rigid foams in various high-volume construction application will result.

Non-cellular applications for polyurethanes which included coating, elastomers, fibers, etc. are largely based in TDI. Urethane adhesives tend to be based on other isocyanates, including some of the specialized types. In the United States, non-foam applications for isocyanates represent less than 10% of the total isocyanate consumption.

C. Application Technology-Urethane Systems

The manufacture and sale of polyurethane products is a relatively sophisticated industry that relies heavily on specific formulations and applications knowhow. This has tended to restrict the growth of polyurethanes in areas of the world where:

(a) there has been no local production of isocyanates and specialty polyols and

(b) there may be insufficient knowhow and technical service capability to develop and market urethane foam systems to the local industry.

In emerging markets, the cost of urethane foams as compared to natural materials has hampered and will continue to restrict the development of urethane foam industries. However, the tremendous versatility of flexible and semi-rigid cellular products in particular will provide a base for the growth of local urethane industries. This has been demonstrated by the rapid acceptance of polyurethane products and more specifically mattresses in Japan over a relatively short period in the early 1960's.

D. Isocyanate Technology

The two most important isocyanate products are TDI and PMPPI. Table 3 indicates the current and projected relative market size for the isocyanate materials, on a worldwide basis. The increased importance of PMPPI type product in the isocyanate consumption pattern is evident as the market share of these materials will increase from 22 to 33 % by 1980. The current isocyanate position in Western Europe is indicated in Figure 3. In each of the countries, TDI accounts for between 55 and 90 % of the total

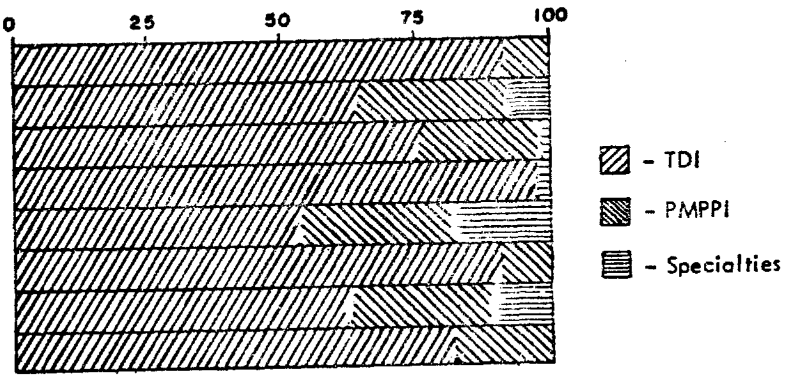


Fig. 3 Relative Importance of Different Isocyanates by Country (percentage)

isocyanate demand, with the PMPPI market varying up to 25 % and that for the "specialty isocyanates" averaging 5-10 %. The analysis in this paper will be limited to these two isocyanates, since they are the most likely candidates for commercialication in Korea.

Tolylene diisocyanate technology and manufacture is dominated on a worldwide basis by Allied Chemical, E. I. DuPont, Bayer and ICI. Major factors in PMPPI production technology included Upjohn, Bayer and ICI. Although Mitsubishi Chemical and Nippon Soda developed their own TDI processes, isocyanate knowhow employed in Japan has largely been based on technology licensed from one of the above firms. New potential manufacturers can anticipate licensing technology for the manufacture of tolylene diisocyanate Knowhow for PMPPI production, however, is more tightly held and extremely difficult to license. Bayer and ICI have limited the licensing of their technology to joint ventures in which they are involved. With the increased likelihood of PMPPI manufacture in a developing market, a shift in this licensing posture should be evident.

Table 3. Isocyanate Demand

	1971		1980	
	MT	%	MT	%
TDI	335,000	72	865,000	60
PMPPI	102,800	22	474,000	33
Others*	28,000	6	100,000	7
	465,800	100	1,439,000	100

*Includes MDI, HMDI, MCHI, XDI, HXDI, HMDI Biuret, DMBDI, BTDI, ODI, NDI and various TDI isomers.

1. Tolylene Diisocyanate (TDI)

Tolylene diisocyanate is manufactured by the phosgenation of tolylene diamine (TDA) in an orthodi chlorobenzene solution at 80°C and atmospheric pressure. The diamine is produced by the reduction of an 80/20 weight percent mixture of the 2,4/2,6 isomers of dinitrotoluene (DNT). The primary reactions for TDI manufacture are illustrated in Figure 4. A schematic flowsheet for the phosgenation of TDA is outlined in Figure 5. The TDI isomer distribution can be modified by distillation to give a specialty product.

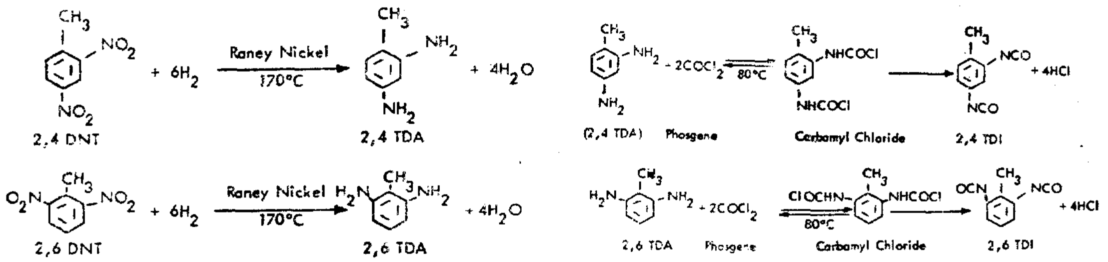


Fig. 4 Principall Reactions for TDA and Tdimanufacture
a) Toylene Diamine (TDA) b) Tolylene Diisocyanate (TDI)

Table 4 Japanese Isocyanate Capacity ('000MT/yr) July 1972

	TDI	PMPPI	Technology
Mitsubishi Chemical Kurosaki	9.0	—	Mitsubishi
Mitsui Toatsu Omuta	10.0	3.6	Du Pont
Nippon Polyurethane Tokuyama	13.0	12.0	TDI-Bayer PMPPI-Hodogaya
Nippon Soda Takaoka	6.0	—	Nippon Soda
Sumitomo Bayer Niihama	7.0	7.2	Bayer
Takeda Tokuyama	7.3	—	Allied
	52.3	22.8	

On a world scale, a typical new TDI plant would have a capacity of approximately 45,000 metric tons per year. However, Japanese plants are still considerable smaller. (See Table 4). Mitsubishi Chemical's 9000 metric ton plant has two 4,500 ton reaction trains. It is reasonable to assume that future Japanese plants will be close to 25,000 metric tons, but no plant of this capacity has as yet been announced.

In considering the construction of TDI facilities, a number of alternatives can be selected with respect to degree of backward integration. Although some companies (e.g. Bayer, Mobay, Du Pont) have totally integrated complexes and produce dinitrotoluene, carbon monoxide, hydrogen and nitric acid, others purchase the dinitrotoluene starting material. With the announced project of Air Products, tolylene diamine is also becoming available as a commodity. The lowest capital investment case, therefore, involves the production of phosgene and the subsequent phosgenation of TDA to TDI. The economics presented in Table 5 are however, based on the use of purchased dinitrotoluene, and provide for phosgene generation and the recovery of by-product HCI for a TDI plant with an annual production rate of 15,000 metric tons. The calculated transfer price of 33.3 cents/lb compares to a current world market price for TDI of 29 cents/lb.

Productions of TDI lends itself to integration with a fertilizer complex in that:

(a) nitric acid can be used to produce dinitrotoluene
(b) spent sulfuric acid can be used within the fertilizer plant and
(c) carbon monoxide and hydrogen available in ammonia reformer gases can be used, to respecitvely produce phosgene and reduce DNT to DNA.

While integrating TDI manufacture with a fertilizer complex may not be feasible, integration backward from TDI production should be evaluated. The investment for an integrated TDI plant with provision for toluene nitration, nitric acid, and gas reformer units is about double that for a TDI plant based on DNT purchased. In the U.S., with large DNT facilities, the transfer prices for TDI manufactured in either a vertically integrated plant or a plant based on purchased DNT are comparable.

2. Polymethylene Polyphenyl Isocyanate (PMPPI)

PMPPI is produced by the phosgenation of polymethylene polyphenyl amine (PMPPA) in a monochlorobenzene solvent. The amine is an aniline-formaldehyde condensation product. At least two processes can be used to synthesize the PMPPA precursor, but the phosgenation step is similar in both cases. The reactions leading to PMPPI are given in Figure 6. Although the phosgenation flowsheet is relatively similar to that for TDI (Figure 5), the processing conditions reflect the physical properties of the polymeric material. The annual capacity of the newest PMPPI plants in Western Europe and the U. S. are in the range of 25-30,000 metric tons. The largest Japanese plant is 12,000 MT. Yr (see Table 4).

Table 5 Production Cost estimate Tolylene Diisocyanate From Dinitrotoluene

Basis: Location-Japan
Capacity-33 MM lb/yr (15,000 MT/YR)
Rate-8,000 Hr/Yr

Capital Cost	$MM
Battery Limits Capital Cost	7.5
Offsites Capital Cost	3.0
Total Fixed	10.5
Working	2.1
Total Fixed and Working	12.2

RAW MATERIALS	QUANTITY	UNIT	PRICE*	CENTS/LB. TDI	
Dinitrotoluene	1.28	LB/LB	7.7	9.86	
Hydrogen	.12	LB/LB	6.1	1.46	
Chlorine	.96	LB/LB	2.5	2.40	
Carbon Monoxide	.55	LB/LB	3.1	1.71	
Methanol	.01	LB/LB	2.0	0.02	
ODCB	.01	LB/LB	15.0	0.15	
Nickel Catalyst	.002	LB/LB	250.0	0.50	
Misc. Chemicals				0.13	
HCl 32 Wt. %**	2.94	LB/LB	0.32	(0.094)	
NET RAW MATERIALS;					15.29
UTILITIES;					
Power	0.65	KWH/LB	1.4	0.91	
Cooling Water	0.17	MGal/LB	2.1	0.36	
Steam	0.013	MLB/LB	88	1.14	
Nitrogen				0.01	
TOTAL UTILITIES COST;					2.42
OPERATING COSTS;					
Labor-4 men/shift					
Supervision-1 Foreman/shift & Supervisor					
Maintenance Material and Labor @4%BLCC					
TOTAL OPERATING COSTS;					1.36
OVERHEAD EXPENSES;					
Direct Overhead-30% (Labor & Supervision)					
General Plant Overhead-65% Operating Costs					
Insurance, Property Taxes-1.5% Total Fixed Investment					
Depreciation-(Basis:10% BLCC+5% Offsites)					
Interest-8% on Working Capital					
TOTAL OVERHEAD EXPENSES;					4.74
TOTAL COST OF PRODUCTION;					23.81
RETURN 30% ON TOTAL FIXED INVESTMENT;					9.54
TRANSFER PRICE;					33.35

*—¢/unit

Economics for the production of 10,000 MT. Yr. of PMPPI, based on aniline as the starting material and using the conventional route, are given in Table 6. The calculated PmPPI transfer price, with a 30% pretax return on total investment, is 27.6 cents/lb. This compares with a current world price of 30.5 cents/lb. for this material. While this may appear favorable, market development expenses for PMPPI tend to be higher than conventional large volume intermediates and an additional 2-3¢/lb. must be allocated for costs.

E. Polyol Technology

The basic raw material for essentially all urethane polyols is propylene oxide. Three process routes are used to make this material of which only two, the chlorohydrin process and the Oxirane process are commercially important. Since the latter route is proprietary to Atlantic Richfield and Halcon Interna-

Table 6. Production Cost Estimate PMPPI ex Aniline (Conventional Route to PMPPA)

	Capital Cost	$MM
Basis: Location-Japan	Battery Limits Capital Cost	3.9
Capacity-22 MM lb/yr (10,000 MT/yr)	Offsites Capital Cost	1.6
Rate-8000 hrs/yr.	Total Fixed	5.5
	Working	1.3
	Total Fixed and Working	6.8

RAW MATERIALS	QUANTITY	UNIT	PRICE*	CENTS/LB.	PmPPI
Aniline	0.97	Lb/Lb	0.5	8.30	
Formaldehyde (37%)	0.41	Lb/Lb	1.8	0.74	
Chlorine	0.66	Lb/Lb	2.5	1.65	
Carbon Monoxide	0.27	Lb/Lb	3.1	0.84	
NaOH (at 50%)	0.76	Lb/Lb	1.5	1.14	
Other Chemicals				0.50	
HCl (at 32%)**	0.60	Lb/Lb	0.32	(0.19)**	
NET RAW MATERIALS:					12.98
UTILITIES:					
Power	0.47	KWH/Lb	1.4	0.66	
Cooling Water	0.11	Mgal/Lb	2.1	0.23	
Steam	0.005	Mlb/Lb	88	0.44	
Nitrogen				0.25	
TOTAL UTILITIES COST:					1.58
OPERATING COSTS:					
Labor 4 men/shif					
Supervision 1 Foreman/shift & Supervisor					
Maintenance Material and Labor @ 4% BLCC					
TOTAL OPERATING COSTS:					1.41
OVERHEAD EXPENSES:					
Direct Overhead-30% (Labor & Supervision)					
General Plant Overhead-65% Operating Costs					
Insurance, Property Taxes-1.5% Total Fixed Investment					
Depreciation-(Basis: 10% BLCC+5% Offsites)					
Interest-8% on Working Capital					
TOTAL OVERHEAD EXPENSES:					4.10
TOTAL COST OF PRODUCTION:					20.07
RETURN 30% ON TOTAL FIXED INVESTMENT:					7.50
TRANSFER PRICE:					27.57

*-¢/unit

**-By Product

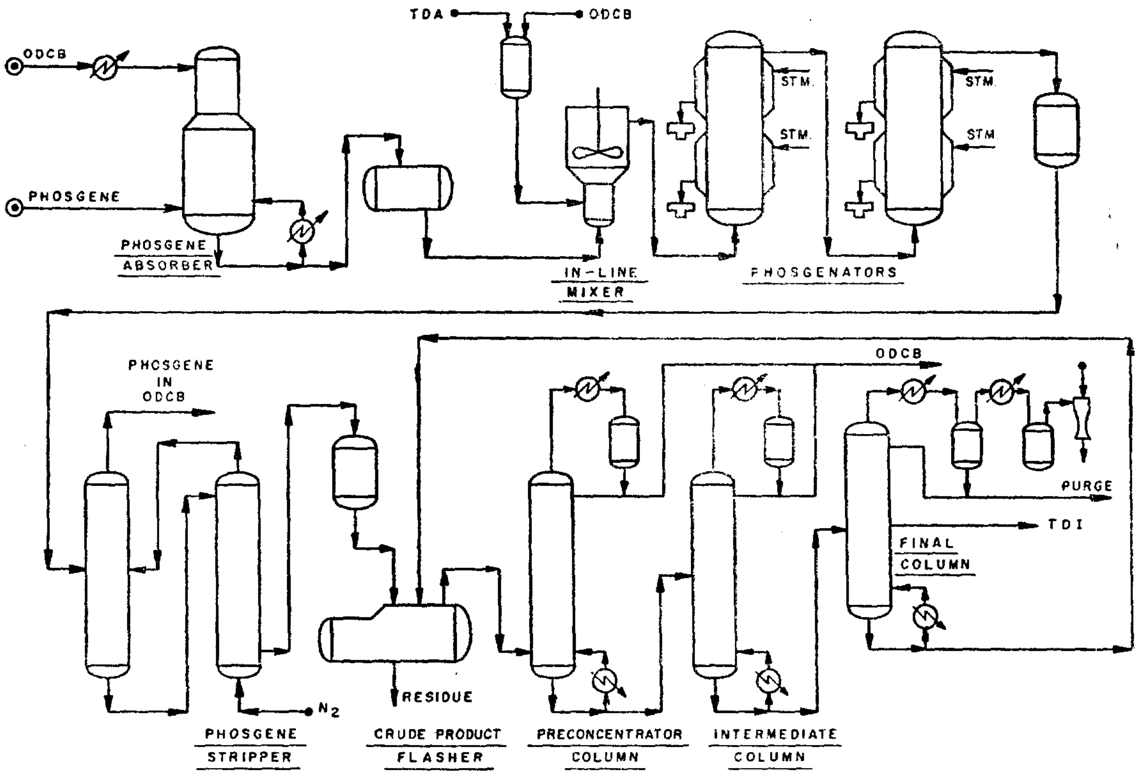
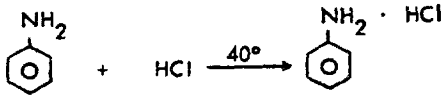
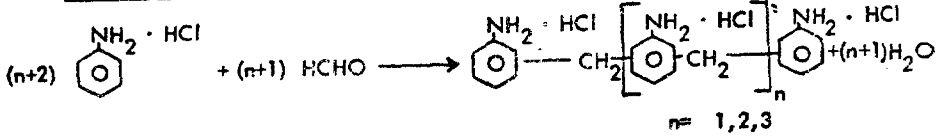


Fig. 5.

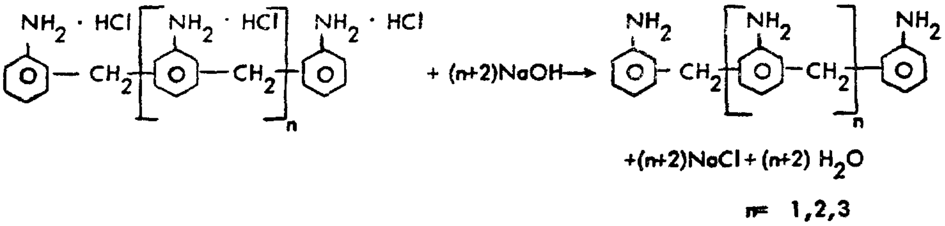
1. Aniline Hydrochloride



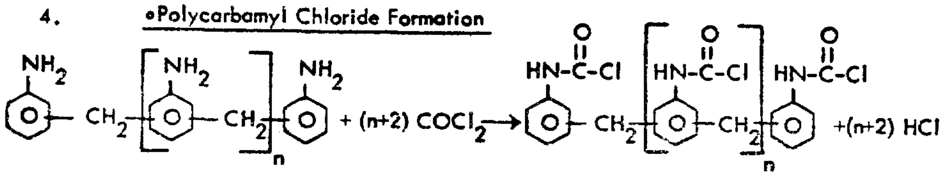
2. PMPPA - Hydrochloride



3. PMPPA Formation

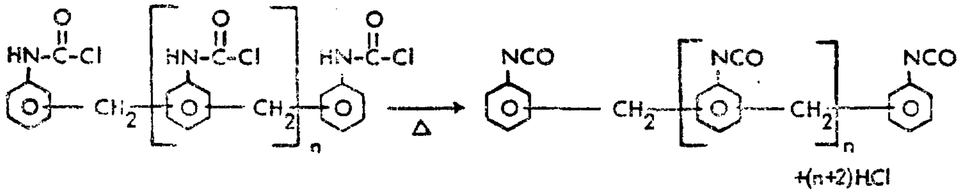


4. **Polycarbamyl Chloride Formation**



n= 1,2,3

5. **PMPPI Formation from Polycarbamyl Chloride**



n= 1,2,3

Fig. 6 Process Chemistry Polymethylene Polyphenyl Isocyanate

Table 7. Production Cost Estimate Propylene Oxide Chlorohyrin Process

	Capital Cost	$MM
Basis: Location-Japan	Battery Limits Capital Cost	2.7
Capacity-44 MM lb/yr (20,000 MT)	Offsites Capital Cost	1.1
Rate-8,000 Hr/Yr	Total Fixed	3.8
	Working	0.9
	Total Fixed and Working	4.7

RAW MATERIALS	QUANTITY	UNIT	PRICE*	CENTS/LB PO	
Propylene 92%	0.925	Lb/Lb	2.7	2.50	
Chlorine	1.40	Lb/Lb	2.5	3.50	
Lime	1.33	Lb/Lb	0.6	0.80	
Catalyst and Chemicals				0.05	
Propylene Dichloride**	0.1	Lb/Lb	1.5	(0.15)	
Calcium Chloride**	2.6	Lb/Lb	nil		
TOTAL RAW MATERIALS:					6.70
UTILITIES:					
Power	0.1	KWH/lb	1.4	0.14	
Cooling Water	0.04	MGal/Lb	2.1	0.08	
Process Water	0.007	MGal/Lb	25	0.18	
Steam	0.005	MLb/Lb	88	0.44	
TOTAL UTILITIES COST:					0.84
OPERATING COSTS:					
Labor 3 men/shift Supervision-1 Foreman/shift & Supervisor Maintenance Material and Labor @ 4% BLCC					
TOTAL OPERATING COSTS:					0.54
OVERHEAD EXPENSES:					
Direct Overhead-30% (Labor & Supervision) General Plant Overhead-65% Operating Costs Insurance, Property Taxes-1.5% Total Fixed Investment Depreciation-(Basis: 10% BLCC+5% Offsites) Interest-8% on Working Capital					
TOTAL OVERHEAD EXPENSES:					1.24
TOTAL COST OF PRODUCTION:					9.32
RETURN 30% ON TOTAL FIXED INVESTMENT:					2.59
TRANSFER PRICE:					11.91

*-c/unit **-Byproduct Credit

tional and has never been for license to a third party, only the chlorohydrin process will be considered.

Over 75% of the world's capacity is based on this process and plants are still being constructed using this technology (e.g. Dow Chemical in Stade, Germany and Santos, Brazil as well as other ventures in Eastern Europe). Table 7 outlines economics for a plant having a capacity of 20,000 metric tons per year. Propylene oxide produced in this plant would have a transfer price of 11.9 cents/lb. If a chlorohydrin-based propylene oxide plant is to evaluated for Korea, careful consideration should be devoted to environmental problems resulting from plant effluent containing calcium chloride and various organic by-products. Sodium hydroxide may be used instead of lime to alleviate this problem.

A. It would be necessary to import several specialty polyhydric alcohols to produce the required polyols. Chlorohydrin technology is readily available for license from operating companies which would include Nippon Soda, Jefferson Chemical, Olin, ICI and Union Carbide.

The above companies will also generally license knowhow for the production of polyethers polyols and the formulation of the various polyurethane foam systems. A typical multi-purpose batch plant for the production propylene oxide based polyethers is shown in Figure 7. The transfer price for conventional polyether polyols, based on 11.9 cents. lb, propylene oxide would be approximately 18.0-18.5 cents/lb.

In summary, polyurethane intermediates production on a relatively large scale could be contemplated in Korea with licensed knowhow. The specific timing for the commercialization of these ventures is dependent on a careful assessment of local markets, production economics, and priorities for other petrochemical projects.

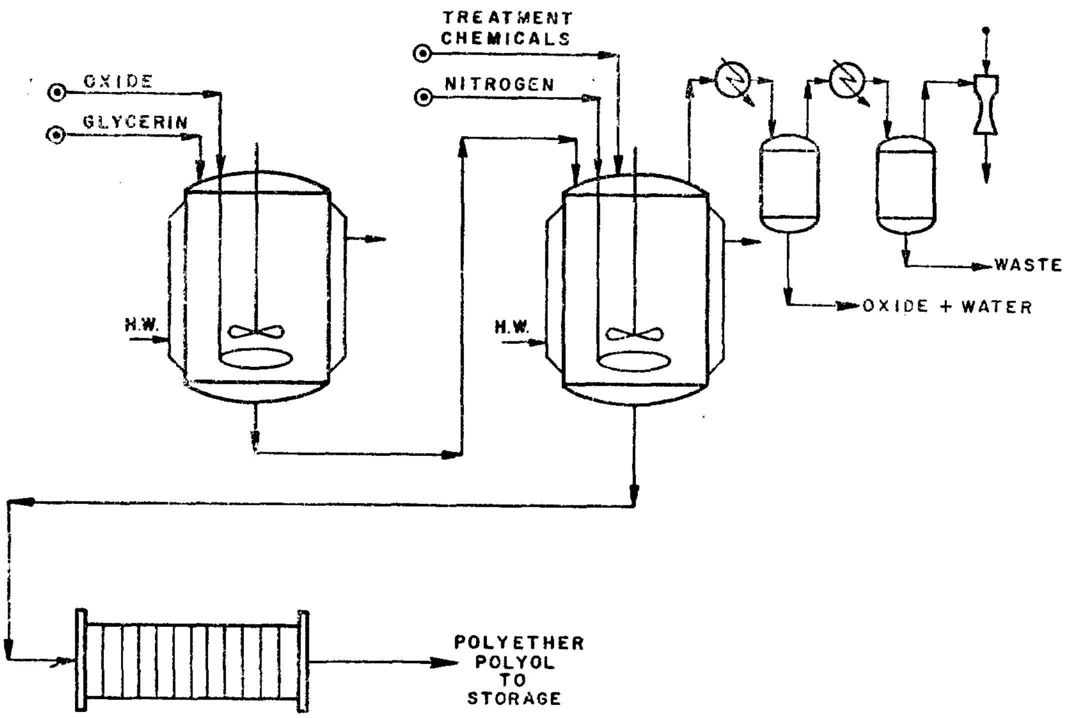


Fig. 7