

**Annex I**

**The Demonstration Project of Wanhua Rongwei Formulated Polyols  
with Premixed Cyclopentane Blending Center**

**Safety Assessment Report**

**(The First Draft)**

**Nanjing Forest University**

**August 2010**

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## **Introduction**

In November 2009, the 59<sup>th</sup> meeting of “Montreal Protocol” Multilateral Fund Executive Committee approved a demonstration project of formulated polyols with premixed cyclo-pentane blending center in the polyurethane foam sector in China. To promote the smooth implementation of this demonstration project and cooperate with the preparation of the HCFC Phase-out Plan in the Polyurethane Foam Sector, the Foreign Economic Cooperation Office of the Ministry of Environmental Protection has initiated a technical assistance project of safety assessment of premixed cyclo-pentane and formulated polyols production, transportation and use.

The main objectives of the project are to: Carry out comprehensive studies and researches in producing, transporting and handling of blended polyols containing pentane; Test the safety data of blended polyols containing cyclo-pentane to provide a reference for the production, transportation, use and other sectors; Evaluation of Wanhua Rongwei and [Minea Electrical Appliance's existing facilities, and give the recommendations on the reform plan; Compile Material Safety Data Sheet\(MSDS\) for blended polyols containing cyclo-pentane; Formulate the Safety Assessment Report on producing, transporting and using of blended polyols containing cyclo-pentane to guide operators in various sectors.](#)

### **1. Technical Feasibility Analysis of Cyclopentane Substitution**

After CFC-11 was eliminated, the refrigerator sector in China has been using cyclo-pentane as a physical foam blowing agent in the production of polyurethane foam. Compared with HFC, cyclo-pentane has a low global warming potential (GWP) with zero ozone depletion potential (ODP). It has a short lifecycle in the atmosphere and can truly meet the requirements of environmental friendly and fluorine-free. In the long run cost perspective, cyclopentane is the lowest cost alternative currently available. China has domestic cyclopentane production with low price; in terms of technology, there is extensive support from a large number of combined materials suppliers. Polyurethane foam can obtain good insulation properties under low density conditions by using cyclopentane as the foaming agent. Therefore, considering environmental and economic benefits, cyclopentane technology is considered as the final solution for most rigid polyurethane foam applications to replace HCFC-141b.

Cyclopentane is an alicyclic hydrocarbon with weak polarity, having poor solubility in most polyether polyols, therefore, compatibility between cyclopentane and polyether is the key technical issue to be solved when using cyclopentane as blowing agent. The compatibility can be improved in two ways, enhancement of the polyether structure and adding foam stabilizer.

### 1.1 Polyether polyols

The performance of polyether polyols has a close relationship with the starting agent and also related to the length of molecular chain and arrangement structure of oxidized olefin. There is a large variety and complex species of starting agents for polyether polyols synthesis; however, according to the distinction of active group nature, the initial agents for polyether polyols synthesis mainly include two categories, hydroxyl containing compounds and amine containing compounds. The most commonly used initial agents are propylene glycol, trimethylolpropane, glycerol, mannitol, sorbitol, pentaerythritol, sucrose, xylitol, ethylene diamine, triethanolamine, toluene diamine. In addition, aromatic polyether uses compounds such as bisphenol A, phenol - formaldehyde condensate, aniline - formaldehyde oligomers, 3 (hydroxyethyl) isocyanurate or the compounds of common starting agents. To obtain polyether polyols with appropriate nature of functionality and viscosity, etc, sometimes mixed starting agents are used for polyether production.

To address the solubility problems of cyclopentane in polyether, the polyether structure is usually improved to enhance the solubility of cyclopentane with low polarity in polyether. The selection of starting agent, polyether functionality, hydroxyl value and polyether water content, etc, will influence the cyclopentane solubility. Huntsman Company (former ICI Polyurethane) made detailed experimental study on the solubility of some polyethers, with the results shown in Table-1, both starting agents and hydroxyl values having some impact on cyclopentane solubility.

**Table-1 The solubility of cyclopentane in some major polyethers**

Polyol type	Hydroxyl value mgKOH/g	c-P solubility in polyols %
Sucrose polyether	440	16

Sucrose polyether	310	48
Sorbitol polyether	490	19
Glycerol polyether	540	18
Aromatic polyether	500	12
Aliphatic polyester	250	8
Aromatic polyester	347	2

Currently, there are a lot of polyethers used for cyclopentane foaming system in China; Manufacturers such as Guangdong Wanhua Rongwei, Nanjing HBL, Shandong Dongda have the product grades for cyclopentane foaming.

**Table-2 Domestic representative polyethers for rigid foam**

Supplier	Grade	Purpose
Guangdong Wanhua Rongwei	Wanefoam RCI36 series Wanefoam RCI36 series Wanefoam RCI36 series	Insulation materials of refrigerator and cold storage, etc.
Nanjing HBL	<a href="#">H563</a> <a href="#">H539</a> <a href="#">H577</a> H566	Insulation materials of refrigerator and freezer, etc.
Shandong Dongda	DCP-401 DCP-402	Insulation materials of refrigerator cold storage and freezer, etc

## 1.2 Foam stabilizer

In the process of plastic polyurethane foam, stabilizer is an indispensable assistant, it plays a role of foam material emulsion, foam stabilization and cell regulation, while increasing the component solubility.

The currently used foam stabilizers are mostly silicone surfactants; its main structure is polysiloxane-olefin oxide block copolymer, commonly known as “silicone oil” (note: they are not real silicone oil). There are a number of silicone foam stabilizers; the foam stabilizers for the foaming system of different flexible foams, rigid foams and HR foam have different structures,

generally containing duplicate dimethyl siloxane segment, ethylene oxide segment and propylene oxide segment.

In the block copolymer, olefin polymer oxidation is a hydrophilic segment and polysiloxane is a hydrophobic segment; therefore, they can well mix and emulsify each component into a homogeneous system and enable various reactions to process in balance. It can meet different production requirements by regulating relative molecular mass, functionality and polyether copolymer, etc. Changing the proportion and arrangement sequence of ethylene oxide polymers and propylene oxide polymers in polymer segment, regulating the polarity of foam stabilizers can change the foam stabilizer emulsifying performance thereby improve the solubility of cyclopentane in polyether.

Currently, there are a number of foam stabilizer grades in the market, the customer can choose suitable foam stabilizer according to different foaming system. Foam stabilizers such as the B8510 and B8462 of German Evonic, the DC5580 and DC5598 of Air Products, L-6840 of Momentive, as well as AK8830 and AK8818 of Nanjing Dymatic Shichuang Co., Ltd can be used for cyclopentane foaming system.

In actual production and application, according to the actual application, improve polyether structure and select suitable foam stabilizer to make formulated polyols form a stable and homogeneous system thereby improve the storage stability of mixed components.

### **1.3 Stability testing of premixed formulated polyols**

There are a number of polyols suppliers in China that provide dry formulated polyols for cyclopentane foaming system. We conducted sampling and require 6 manufacturers, namely, Guangdong Wanhua Rongwei, Jiangsu Lvyuan, Nanjing HBL, Shandong Dongda, Changshu Yitong and Jiangyin Youbang, to provide 16 representative grades of dry formulated polyols for the downstream customers that using cyclopentane foaming system. We prepared the collected polyols into samples with different contents of cyclopentane in the laboratory and entrusted Jiangsu Research Institute of Product Quality Supervision and Inspection to carry out test on stability of the samples. The prepared formulated polyols were put into test tubes and sealed, the storage stability in different temperatures were tested, The formulated polyols with good compatibility have high system storage stability and no stratification occurred in low temperatures. The test temperatures are -5°C, 0°C, 5°C, 10°C, 15°C, 20°C and 25°C respectively.

It is observed whether there is stratification after 48h's storage in each temperature to judge its stability. The selected mass ratio of formulated polyols and cyclopentane are 100:13 and 100:15, which currently are equivalent or even higher than the rates of using of blended polyols with cyclo-pentane as blowing agent.

**Table-3 Stability test of cyclopentane formulated polyols (the mass ratio of formulated polyols and cyclopentane is 100:13)**

Product serial No.	Test Results						
	25°C	20°C	15°C	10°C	5°C	0°C	-5°C
WH 1#	A little turbid	Turbid	Turbid	Turbid	Turbid	Stratified	
WH 2#	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified
WH 3#	Turbid	Turbid	Turbid	Turbid	Turbid	Stratified	
WH 4#	Turbid	Turbid	Stratified				
WH 5#	Transparent	A little turbid					
LY(XF)	A little turbid	Turbid	Turbid	Turbid	Turbid	Stratified	
LY(HR)	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Hongbaoli H524	Transparent	Transparent	Transparent	Transparent	Stratified		
Hongbaoli H543	Transparent	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified
Dongda 1#	Transparent	Transparent	Transparent	Transparent	Stratified		
Dongda 2#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Dongda 3#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Yitong 3018	Turbid	Turbid	Turbid	Turbid	Stratified		
Yitong 3030	A little turbid	Stratified					
Youbang 1#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Youbang 2#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	

**Table-4 Stability test of cyclopentane formulated polyols (the mass ratio of formulated polyols and cyclopentane is 100:15)**

Product serial	Test Results
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No.	25°C	20°C	15°C	10°C	5°C	0°C	-5°C
WH 1#	A little turbid	Stratified					
WH 2#	Transparent	A little turbid	A little turbid	A little turbid	A little turbid	Stratified	
WH 3#	Turbid	Turbid	Turbid	Stratified			
WH 4#	Turbid	Turbid	Turbid	Stratified			
WH 5#	Turbid	Turbid	Turbid	Turbid	Turbid	Stratified	
LY(XF)	Turbid	Turbid	Turbid	Turbid	Turbid	Stratified	
LY(HR)	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Hongbaoli H524	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Hongbaoli H543	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Dongda 1#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Dongda 2#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Dongda 3#	Transparent	Transparent	Transparent	Transparent	Stratified		
Yitong 3018	Turbid	Turbid	Stratified				
Yitong 3030	A little turbid						
Youbang 1#	Transparent	Transparent	Transparent	Transparent	Transparent	Stratified	
Youbang 2#	Transparent	Stratified					

Table-3 and Table-4 shows the results of stability test. It is shown that most stratification of the 16 grades of formulated polyols occurs at 0°C, with good stability. Only a handful of samples have poor compatibility with cyclopentane, with high stratification temperature. This is showing that the domestic polyether suppliers have basically solved the compatibility issue of cyclopentane and polyether. In the sample test of Wanhua Rongwei, the 5# sample (Mass ratio of formulated polyether and cyclopentane is 100:13) has outstanding stability without stratification at -5°C, indicating good compatibility of polyether and cyclopentane; meanwhile, also proving Wanhua Rongwei can technically solve the compatibility issue.

## 2 Safety Test of Formulated polyols with premixed cyclopentane

Cyclopentane is a highly flammable chemical; its vapor can form explosive mixture with air, easy to burn and explode with open flame and heat. Strong reaction will occur when contacting with oxidants, or even cause combustion, so the heated containers have explosion hazard. Its vapor is heavier than the air, can spread afar at a low height, and will cause an explosion when meets fire.

Polyether is a flame retardant chemical, while the hazard of formulated polyols will significantly increase after adding the highly flammable and explosive cyclopentane; there are more strict requirements on the security measures of premixed cyclopentane and formulated polyols production, storage and use; therefore, it is necessary to test the security data of formulated polyols with premixed cyclopentane so as to assess the overall security.

**Table-5 The physical and chemical properties of cyclopentane**

Melting point(°C):	-93.7
Boiling point (°C):	49.3
Relative density (water = 1):	0.75
Relative vapor density (air = 1):	2.42
Saturation vapor pressure (kPa):	53.32(31)
Heat of combustion (kJ / mol):	3287.8
Critical temperature (□):	238.6
Critical pressure (MPa):	4.52
Logarithm value of octanol / water partition coefficient values:	7 (calculated value)
: Flash point (°C):	-25
Ignition temperature (°C):	361
Explosive limit(volume)	1.4%~8.0%
Solubility:	Insoluble in water, soluble in most organic solvents such as in alcohol, ether, benzene, carbon tetrachloride, acetone, etc.

## 2.1 Test of flash point

Flash point means, in specified conditions, heat the flammable liquid to the minimum temperature of instant ignition caused by the contact of its vapor and flame. Flash point is divided into open flash point and closed flash point; without specification, the general flash point is closed flash point. The hazardous levels of flammable liquid are classified according to the closed flash point. The fire hazard of flammable liquid can be identified according to the flash point, having great significance in production and application. Flash point is an item showing flammable liquid evaporation tendency and security nature. The hazardous levels of flammable liquid are classified according to the flash point; these with closed flash points below 45℃ are called flammable products and these above 45℃ are called combustible products.

In specified conditions, heat cyclopentane formulated polyols, when the oil temperature reaches a certain point, the vapor of cyclopentane formulated polyols mixes with the surrounding air; once contacting flame, flash fire phenomenon will occur; the minimum flash fire temperature is the flash point of formulated polyols with cyclopentane.

The equipments for flash point test must be in line with the existing national flash point testing standards; the current national standard of open flash point is GB/T 3536-2008 Petroleum products—Determination of flash and fire points—Cleveland open cup method; and that of the closed flash point is GB/T261-2008 Determination of flash point—Pensky-Martens closed cup method. The SYD3536 Cleveland open flash point instrument and SYD261 closed flash point instrument of Shanghai Changji Geological Instrument are selected for the open flash point test and closed flash point test.

**Table-6 Open flash point of formulated polyols with cyclopentane (Unit: °C)**

Product	Mass ratio of fomulated polyether and cyclopentane					
	100:5	100:7	100:9	100:11	100:13	100:15
Serial No.						
WH 1#	—	—	55	51	45	43
WH 2#	—	—	54	51	46	40
WH 3#	—	—	57	49	46	42
WH 4#	—	—	53	46	43	42
WH 5#	—	—	56	47	44	42
LY(XF)	—	—	49	46	42	37

LY(HR)	—	—	51	45	42	39
Hongbaoli						
H524	—	—	50	46	42	40
Hongbaoli						
H543	—	—	57	49	41	38
Dongda 1#	—	—	54	49	39	32
Dongda 2#	—	—	54	50	41	34
Dongda 3#	—	—	56	50	42	37
Yitong 3018	—	—	55	52	48	42
Yitong 3030	—	—	57	50	46	43
Youbang 1#	—	—	56	48	45	40
Youbang 2#	—	—	55	46	44	40

**Table-7 Closed flash point of formulated polyols with cyclopentane (unit: °C)**

Product	Mass ratio of formulated polyether and cyclopentane					
	100:5	100:7	100:9	100:11	100:13	100:15
Serial No.						
WH 1#	26	25	12.7	8.7	6.3	0.7
WH 2#	21.7	15.7	13.3	8.3	4	-0.7
WH 3#	20.7	16.7	14.3	8.3	6	0.7
WH 4#	19	14.3	10.3	7.3	3.7	1.3
WH 5#	22	16.3	12.7	10	1.3	0
LY(XF)	22.3	14	9.7	10	4.3	1
LY(HR)	20.7	17.7	15.7	10.7	5.7	0.7
Hongbaoli						
H524	14	12	11.3	11	0	-1.7
Hongbaoli						
H543	14	12.3	11	6.3	4	-1.3
Dongda 1#	12.3	10	8.7	7	2.3	-2.3
Dongda 2#	12.3	9	7.7	6	0	-2.3
Dongda 3#	10.7	9.3	5.3	4.3	3	-1.3
Yitong	15.7	13.3	11.3	8	5	3

3018						
Yitong						
3030	14.3	11.3	8	5.7	-3	-5.3
Youbang						
1#	17	13.3	11	6	3	-1
Youbang						
2#	16.7	10	6	3	1.7	0

With the increasing content of cyclopentane, the flash point of formulated polyols decreased, the flammability is significantly increased; therefore, high requirements are put forward on the security measures in production. The open flash test is largely subjected to the environmental factors; in well-ventilated environment, the volatile cyclopentane vapor has fast diffusion speed, therefore, the measured figure is usually high. It shows that in the storage of formulated polyols with premixed cyclopentane, it is necessary to ensure a well-ventilated storage workshop. Closed flash point is mainly used to assess the security level of flammable liquid; according to the test results, it can be confirmed the security level of formulated polyols with premixed cyclopentane is **class II flammable liquid**, thereby the safety standard, transportation and storage requirements are determined on this classification.

## 2.2 Vapor pressure test

Vapor pressure refers to the vapor of the substance on the surface of the liquid or solid; the pressure generated by such vapor on the liquid (or solid) surface is known as the liquid (or solid) vapor pressure. Some molecules with kinetic energy from the liquid at a certain temperature keep on escaping from the liquid surface and become vapor; this process is known as evaporation; meanwhile, some vapor molecules return to the liquid and this process is called condensation. When the rate of evaporation is the same as that of condensation, the dynamic equilibrium is achieved; the vapor pressure is the liquid saturated vapor pressure at such temperature.

The vapor pressure of formulated polyols with premixed cyclopentane is primarily generated by cyclopentane vapor; test the vapor pressure data of formulated polyols to determine the storage standards of formulated polyols with premixed cyclopentane. The test material is the formulated polyols (Mass ratio of formulated polyether and cyclopentane is 100:15) and the test method is GB/T 21616-2008 Dangerous Goods Test Method for Vapor Pressure of Flammable liquids; that is, directly test the saturated vapor pressure at a certain temperature.

**Table-8 The saturated vapor pressure test of premixed cyclopentane and formulated polyols (Unit: kPa)**

Product serial No.	Test Temperature						
	30°C	35°C	40°C	45°C	50°C	55°C	60°C
WH 1#	48.91	51.35	58.43	68.05	76.27	86.74	92.61
WH 2#	45.9	52.77	59.6	65.12	68.5	78.9	91.67
WH 3#	51.37	58.39	61.61	67.62	76	87.15	96.86
WH 4#	51.34	57.47	63.09	70.35	76.7	87.54	100.18
WH 5#	59.15	62.02	64.32	69.35	78.99	87.44	95.61
LY(XF)	52.32	59.66	63.36	65.48	69.1	72.17	80.13
LY(HR)	58.43	63.64	65.77	70.25	80.42	88.96	97.55
Hongbaoli H524	53.9	59.05	63.04	66.17	72.97	78.15	82.54
Hongbaoli H543	51.11	56.32	62.89	69.16	78.1	84.01	92.44
Dongda 1#	47.81	53.5	59.19	66.78	77.76	86.12	89.16
Dongda 2#	50.29	56.07	59.02	66.54	70.81	77.98	84.58
Dongda 3#	50.31	57.64	61.42	68.29	71.81	78.5	85.17
Yitong 3018	50.9	57.55	61.26	68.1	76.39	83.47	89.47
Yitong 3030	52.91	58.16	63.3	67.2	74.82	79.66	90.46
Youbang 1#	51.07	56.48	62.41	68.86	73.78	82.77	92.3
Youbang 2#	50.97	57.32	61.65	66.65	70.53	77.23	85.01

The vapor pressure of formulated polyols is an important reference for determining premixing conditions and storage conditions. According to test results, the sample with the largest saturated vapor pressure is the 4# sample of Wanhua Rongwei; at 60°C, its saturated vapor pressure is 100.18 kPa, close to atmospheric pressure. In the actual production process, equipments such as the pipeline, formulated polyols tank and transportation tank should keep a certain pressure to ensure the safety of production and application process. The packaging of blended polyols with cyclo-pentane can be 200L galvanized metal tanks or 500~1000L pressure steel tanks. If using galvanized metal tanks, the proposed tanks' thickness are not less than 1.22mm. The tanks must be welded assembly to ensure that the tanks can withstand the

pressure of not less than 200kPa. Rongwei Company uses nitrogen 150 kPa pressure packages for formulated polyols tank, which can ensure the safety in transportation.

### 3 The Implementation Program of Wanhua Rongwei Premixed Cyclopentane and Formulated Polyols Production Line Transformation

#### 3.1 Basic conditions

##### 3.1.1 Geographical location (with the map of the plant and surrounding environment)

Guangdong Wanhua Rongwei Polyurethane Co., Ltd is located in the Industrial Zone, Mingcheng Town, Gaoming District, Foshan, Guangdong, in central and southern Guangdong Province, the northwest part of Pearl River Delta area, west Foshan City, with convenient traffic. See the picture below for plant surrounding environment; the project construction site has the security conditions for cyclopentane tank.



##### 3.1.2 Raw materials (source of the substitutes and production raw materials)

Currently, the domestic suppliers such as Foshan Shunde Meilong Cyclopentane Chemical Co., Ltd, Beijing Eastern Acrylic Chemical Technology Co., Ltd and Shenzhen Esson Industrial Co., Ltd, purchase cyclopentane to substitute HCFC-141b.

Polyether polyols raw materials are mainly produced by the companies, with small purchase quantity; catalysts are mainly purchased from Air Products Company, Jiangsu Dajiang Chemical Co., Ltd and Jiangsu Liyang Chemical Co., Ltd, etc; and the silicone surfactants suppliers are Evonik, Momentive and Nanjing Dymatic Shichuang Co., Ltd.

##### 3.1.3 Power supply

The plant has 300kVA transformer, providing normal production electricity.

##### 3.1.4 Water supply

The plant has running water and fire water supply pipes, provided by the municipal supply department.

### 3.1.5 Stream supply

The plant has a 4-tons' boiler, providing steam for normal production.

### 3.1.6 Compressed air

The plant has air compression and nitrogen system, providing gas source for production and nitrogen protection.

**The above basic conditions can meet the requirements of premixed cyclopentane and formulated polyols production.**

## 3.2 Project implementation plans and security measures

### 3.2.1 Overview of production methods

Guangdong Wanhua Rongwei Polyurethane Co., Ltd uses the mixture of cyclopentane and premixed formulated polyols to provide premixed cyclopentane and formulated polyols material for small household electrical appliance enterprises. The cyclopentane and polyols were sent from their storages to the static premix station by pumps; the mixed polyols with cyclopentane were then sent to the mixing tank to continue blending, and then conduct packaging, storage and transportation.

### 3.2.2 Newly added equipments

Wanhua Rongwei plans to prepare a complete set of facilities of premixed cyclopentane combined material; the newly added equipments include:

**Table-9 List of the newly added equipments**

No.	Type of Equipment	Piece (set)
1	Tank for Cyclopentane 35m <sup>3</sup>	1
2	Pump for Cyclopentane	2
3	Tank for dry combined polyols	2
4	Pump for dry combined polyols	2
5	Premixed device	2
6	Tank for premixed polyols	2
7	Pump for premixed polyols	2

8	Semi-automatic filling machine	2
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At the same time, the company will conduct conversion and retrofitting to power distribution, equip safety, fire prevention facilities and necessary plant civil reconstruction.

### 3.2.3 Electricity, fire and ventilation transformation

#### a. Electricity

In accordance with the process requirements, the production category of workshop transformation is Class A, implement “GB50058-92 Code for Design of Electric Installations within *Explosion* and Fire Hazard Atmospheres” and QB/T2911-2007 Light Industry Standards of the People’s Republic of China. All electrical equipments in the workshop are explosion-proof, and set cyclopentane concentration detectors in special positions during the production process such as cyclopentane storage tank zone, cyclopentane premixed zone, formulated polyols with premixed cyclopentane filling zone and finished goods warehouse of formulated polyols with premixed cyclopentane.

The surplus 30KW of Rongwei Company’s existing 100KW standby diesel generator can meet the application requirements of new projects and ensure the dual power supply requirements of fire and ventilation facilities.

#### b. Fire prevention

According the process requirements, the workshop production category is class A, Cart powder fire extinguishers should be equipped and foam fire hydrant need to be equipped outside of the workshop. Since the workshop is only 2km to Mingcheng fire brigade, the corresponding fire fighting facilities of the fire brigade can be used by the company, an independent foam station is not necessary. According to the equipment layout zone provided by the process, the mixed water is 16t/h and the foam preparation water pipe diameter is  $\Phi 100$ .

Cyclopentane tank water spray cooling, with the water volume of 9.94L/S. Circulating cooling water system needs to be added.

#### c. Ventilation

Workshop transformation should follow the requirement of Class A, the plant should be considered according to the running-through of the first and second floor, all fan motors are explosion-proof.

Building, fire, power supply, electricity and ventilation should implement “GB50016-2006 Architectural Design Code for fire Protection”, “GB50058-92 Code for Design of Electric Installations within *Explosion* and Fire Hazard Atmospheres” and QB/T2911-2007 Light

Industry Standards of the People's Republic of China and apply the safety specifications of cyclopentane foam production of household and similar electrical appliances.

#### 3.2.4 Storage tank for cyclopentane and security measures

Cyclopentane storage system is mainly composed of cyclopentane storage tank, discharge system, liquid level control system, respiratory balance system, electronic control systems and piping system. The newly built cyclopentane storage tank is a 35m<sup>3</sup> pressure vessel with the design and manufacturing in line with national Class II pressure vessel standards; the tank is in double layer and filled with ethylene glycol in the interlayer, for cyclopentane leakage alarm. The newly built cyclopentane tank is planned to place in the vacant original Class A tank zone, which can fully utilize the existing cooling and sprinkler system to ensure the safety of storage and reduce investment cost.

The configuration of each part and technical specifications are as follows:

Tank (inner and outer layer), the connection between the tank and external part by upper and lower flanges and necessary connection accessories; there is a tank support saddle below, and hanging ears in the top for hoisting.

##### a. Cyclopentane storage system technical requirements:

(1) The tank is a Class II pressure vessel, which is designed, manufactured and tested according to the pressure vessel code.

(2) The design and manufacture of pressure vessel are in line with GB150—1998 “Steel Pressure Vessel” and the requirements of “Pressure Vessel Safety Technology Supervision” issued by the Ministry of Labor.

##### b. Discharge system

The discharge system is mainly used to add the cyclopentane in the tanker into the 35m<sup>3</sup> tanks; it mainly consists of the following parts:

- The feeding well equipped with feed control valve and connection hose
- The hose and jaw coupling connecting the tanker discharge port
- Gas replacement hose and jaw coupling connecting the tanker balance port
- Safety valve
- Pneumatic control unit

##### c. Liquid level control system

Float liquid level gauge is used to monitor the tank's liquid level and there is a liquid level display in the control cabinet; when the liquid level is at the highest or the lowest, that is, only

20% left, the electronic control system will alarm, stopping feeding at the highest liquid level and shutting down at the lowest level; 20% liquid level prompts for feeding; the operator should take appropriate measures depending on the circumstances.

Auxiliary tank uses a set of float liquid level gauges to monitor the liquid level in the tank.

The liquid level in discharge system, material transfer system (auxiliary tank), transporting system (main tank) uses automatic control.

d. Hazardous gas monitoring and safety control system

Respectively install 1 hazardous monitoring probe on the cyclopentane tank feeding well and output well, sharing one alarm cabinet; the concentration alarm signals gathered by hazardous monitoring probe will be collected and processed by electrical control cabinet response template.

Alarm parameters setting: the alarm light flashes when the volume fraction of cyclopentane in the air reaches 20% of the lower explosive limit (LEL), and the control cabinet displays the point of failure; up to 40% of LEL, there will be sound and light alarm, the control cabinet will show the failure point; after eliminating failures and conduct necessary maintenance, the operator conducts equipment reset for re-operation.

e. Glycol anti-leakage monitoring alarm system

To monitor the tank cyclopentane leakage, fill the tank interlayer with glycol and set a glycol tank on the top of the storage tank; connect the pipe with the interlayer and install liquid level device on external glycol tank to monitor cyclopentane leakage by the change of glycol liquid level; when the actual level exceeds the set range, the control system will alarm and stop operation, then the operator should take appropriate emergency measures. Glycol is only combustible in case of fire, heat and strong oxidants, and it does not generate safety hazards by itself.

The main tank and auxiliary tank share one set, connected by pipe and ball valve.

f. Respiratory balance and nitrogen intake system

Realized by the balancing valve and saturated device on the tank top, when the main liquid level decreases, the nitrogen forms the saturated gas with the pipeline in the tank by the above-mentioned devices to achieve pressure balance.

The main tank and auxiliary tank share one set, connected by pipe and ball valve.

Once the nitrogen enters the tank by a set of decompression devices; the devices use second decompression to control the inlet pressure within 0.03bar; there is pressure detection sensor and safety valve on the gas inlet device to ensure the pressure within the set range

g. Electrical control system

A set of control systems are used for the automatic control of main tank and auxiliary tank material discharge, transfer, transportation and safety, etc, in cyclopentane filling zone.

h. Internal pipelines and cables

Pipeline system includes the tank's internal cyclopentane pipeline, nitrogen pipeline and compressed air pipeline; argon arc welding is used in cyclopentane pipe welding; leakage test is conducted according to the pressure pipeline code, protective treatment such as antistatic and equipotential grounding are conducted for all pipelines.

Between cyclopentane tank and premixed formulated polyols workshop, cyclopentane transfer pipeline will adopt overhead and single-tube format. Install fire damper on cyclopentane pipeline after entering the workshop and ensure the cyclopentane in the pipeline between fire damper and premixed station to be in high pressure state. Such cyclopentane transfer pipeline meets TUV safety code.

### 3.2.5 Cyclopentane premixed workshop transformation and premixed system

The current workshop of Guangdong Wanhua Rongwei Polyurethane Co., Ltd is in a plant of separate frame. In the general layout, the original workshop was noted with Class A production type, which made construction application and passed the acceptance of the local fire brigade. The transformation is to avail the original workshop and makes appropriate civil reconstruction to ensure the construction in line with the existing national requirements of Class A production workshop of "Architectural Design Code for Fire Protection". The specific transformation measures are as follows:

First, in the original workshop with partition wall, avail some space in the north to block the doorway between the north workshop and south workshop as an anti-explosion wall; meanwhile, avail this space to separate the open staircase, distribution room and control room in south Class A production workshop to meet fire protection requirements.

Second, on separated formulated polyols with premixed cyclopentane workshop, cancel the cement floor of the second floor, retain the structural beams, use gird plate to connect with the first floor thereby facilitate the maintenance of cyclopentane static mixer.

Use static mixer for cyclopentane premixed device. Use dual pneumatic diaphragm pump to send the cyclopentane to the polyol/ cyclopentane premix station; one for standby and one for operation.

Conduct automatic measurement control on the cyclopentane entering premixed system; a German flow meter is installed on the cyclopentane transfer main pipe to conduct accurate measurement on cyclopentane, with the measurement error less than 1%; when reaching the set value, the system will automatically shut down and stop feeding.

Safety facilities of cyclopentane static premix devices: install surrounded house, cyclopentane gas detector and ventilation facilities of explosion-proof motor.

The cyclopentane formulated polyols mixed by static mixer is transported to the 1500L carbon steel jacketed intermediate tank.

**Table-10 Safety measures of the intermediate tank**

Serial No.	Safety device	Quantity (set)	Function	Remark
1	Safety valve	1	Release pressure when tank pressure exceeds the safety limit	
2	Manual exhaust valve	1	Regulate pressure inside the tank	Quick exhaust valve
3	Magnetic sensor	4	<ul style="list-style-type: none"> <li>▲ Minimum alarm: ensure the alarm for minimum raw material in the tank.</li> <li>▲ Start infusion: send signal to the premixed station to start feeding.</li> <li>▲ Stop feeding: stop feeding when reaching the required amount.</li> <li>▲ Maximum alarm: the safety limit of raw material in the tank.</li> </ul>	
4	Manual switching valve	1	Manually control input direction	This set of valves are in close state during maintenance
5	Air pressure indicator meter	1	Indicate air pressure in the tank	
6	Discharge valve	1	Use for discharge or collect raw material samples	
7	Control valve	1	Control raw material adding	
8	Check valve	1	Control raw material input direction	
9	Manual ball valve	1	Connect input pipeline and manually control input	
10	Surrounded pool	1	Collect raw material in accidental leakage	Below the intermediate tank, and the volume is

				1500L, with security alarm device and discharge valve
11	Cyclopentane gas detector	1		
12	Ventilation device	1		Explosion-proof motor

### 3.2.6 Formulated polyols with premixed cyclopentane filling system

Use semi-automatic filling machine with nitrogen facilities; the filling equipment meets the following requirements:

- 1) Weight range:  $\leq 300\text{kg}$  (adjustable); division value: 100g; measurement, review accuracy:  $\pm 0.1\%$  F·S.
- 2) Container standards: 200L galvanized iron barrel (height:  $900 \pm 15\text{mm}$ , diameter:  $590 \pm 15\text{mm}$ ), mass 21kg, pressure  $2.0\text{kg}/\text{cm}^2$ .
- 3) Explosion-proof grade: d □ BT4
- 4) Operating temperature:  $-10 \square - +40 \square$
- 5) Medium temperature:  $\leq 100 \square$
- 6) Material viscosity : $300-1000\text{mpas} / 25 \square$
- 7) Filling the system uses all stainless steel structure; PTFE is used as sealing material, the pressure of nitrogen gas packaging is  $1.5\text{kg}/\text{cm}^2$ .
- 8) The system is equipped with a ventilation interface, effectively removing harmful gas accumulated within the system.
- 9) Ground installation, easy to maintain and operate.
- 10) Below the filling location, install surrounded pool to collect raw material in accidental leakage. The surrounded volume is 200L, with security alarm and discharge valve.
- 11) Install cyclopentane gas detectors.

**Table-11 Intrinsic cyclopentane gas detection and collection device statistics of formulated polyols with premixed cyclopentane transformation project**

Serial No.	Device	Quantity	Installation position	Remark
1	Cyclopentane gas detector	6	▲ Cyclopentane storage tank area (4) ▲ Static mixer (1) ▲ Intermediate tank (1)	
2	Safety box	1	▲ Static mixer	
3	Surrounded pool	2	▲ Static mixer ▲ Intermediate tank	Static mixer surrounded pool should be provided by equipment supplier

**Table-12 The suggestion of adding cyclopentane gas detection and collection device statistics of formulated polyols with premixed cyclopentane transformation project according to the safety assessment**

Serial No.	Device	Quantity	Installation position	Remark
1	Cyclopentane gas detector	4	▲ Filling zone (2) ▲ Finished products warehouse (2)	
2	Surrounded pool	1	▲ Filling zone	

#### **4 Assessment for Transportation Safety of formulated polyols with premixed cyclopentane**

Formulated polyols with premixed cyclopentane is categorized as Grade II flammable liquid referring to the testing result of closed flashing point for formulated polyols with premixed cyclopentane according to standards of public security industry of the People's Republic of China, GA/T 536.1-2005, Grading and test method on fire hazard for flammable and explosive hazards -Part 1: Grading on fire hazard for flammable and explosive hazards. Therefore, formulated polyols with premixed cyclopentane must be managed and transported considering as flammable and dangerous goods. Formulated polyols with premixed cyclopentane transportation must meet the following requirements as specified Regulations on the Control over Safety of Dangerous Chemicals and Regulations on the Control over Dangerous Goods Transportation by Road:

(1) The consignor for formulated polyols with premixed cyclopentane by road transportation must authorize the qualified carrier for dangerous chemicals transportation. The personnel engaging into dangerous chemicals transportation e.g. driving, loading/unloading managing personnel, escorting personnel etc must pass the examination organized by the transportation administration. They can go to their posts upon their qualifications.

(2) The vehicles, vessels, loading/loading machinery and tools shipping formulated polyols with premixed cyclopentane must comply with JT3130-88, Rules of Transportation of Dangerous Goods by Vehicle issued by the Ministry of Communication of the People's Republic of China, passing examination and approval of the road transportation authority. The exhaust gas pipe of the vehicle carrying these goods must be provided with fire retarded device. Don't use the mechanical equipment and tools easily generating sparks when loading/unloading. Apply signs and identification lamps as specified by GB13392-2005, The Vehicle Marks for Road Transportation Dangerous Goods for the vehicles carrying formulated polyols with premixed cyclopentane.

(3) The transportation vehicle shall be provided with approximate types and quantities of fire extinguisher and leakage emergency handling equipment during transportation. The vehicle shall be provided with ground chain and provided with corresponding measures to lash the packaging containers to prevent that the containers from moving during transportation.

(4) Don't load and ship it together with such chemicals as oxidization agent. Avoid direct sunlight, rain, and high temperature during transportation, preferably transported in the morning and in the evening in summer. Keep far away from flame, thermal source, and high temperature zone when pausing.

(5) Drive the vehicle as specified lines when transporting by road. Don't stop it at the residential quarters and the area with high population density. The vehicle shall run at a medium speed. The road transportation distance shall be within 500km for formulated polyols with premixed cyclopentane.

(6) Humping is not allowed for railway transportation, and transport it through containers. It must not be transported with a wooden vessel or cement vessel in bulk way.

## **5 Assessment for Usage Safety of formulated polyols with premixed cyclopentane —Minea Electrical Appliance Co., Ltd, a Demonstrated Project**

Over recent year, some formulated polyols enterprises have tried to properly prepare formulated polyols containing carbon hydrogen foaming agent within formulated polyols enterprises and supply them to the PU foam enterprise for production of foam. Through this technology, the carbon hydrogen foaming agent storage tank and tank farm, the carbon hydrogen foaming agent and dry formulated polyols mixing device which generally set up in PU foam enterprise have been transferred to the formulated polyols production enterprise. Through this technological method, the foam enterprise may supersede HCFC-141b with cyclopentane under a prerequisite that the plant or location is unneeded to be changed. Pre-mixed cyclopentane combination project can solve this problem.

For this project, the pre-mixing capacity is established by Wanhua Rongwei, an upstream enterprise and it prepared for further promotion of pre-mixed cyclopentane combination and then provides pre-mixed cyclopentane combination to the four downstream enterprises such as Minea Electrical Appliance Co., Ltd for purpose of replacing HCFC-141b.

### **5.1 Basic Conditions**

Minea Electrical Appliance Co., Ltd is an enterprise that professionally engages into semi-conductor wine cabinet, semi-conductor refrigerator, semi-conductor beer brewer, and the other semi-conductor refrigerating product.

#### **5.1.1 Raw material**

The alternative technology of this project is to supersede HCFC-141 using cyclopentane as a foaming agent. The formulated polyols containing cyclopentane is directly purchased from Wanhua Rongwei. For purpose of production safety, Minea Electrical Appliance Co., Ltd has purchased formulated polyols with premixed CP of which quantity must be allowed by the fire fighting department each time.

#### **5.1.2 Power supplying facilities**

At present, there is one 260 kVA electric power transformer which has sufficient power supplying capacity and can ensure to meet requirements of implementation. For construction of demonstrated project, the transmission line needs to elevated (with pre-embedded cable) to the

site from the electrical distribution room. This project is provided with limited capacity newly added. Only the existing foaming machine is updated as pentamethylene foaming machine. Furthermore, some exhaust air equipment and carbon hydrogen concentration alarm device.

### 5.1.3 Water supply

This project locates within Tongan Industrial Park, Dongfeng Town, Zhongshan City, Guangdong Province, PRC. There, domestic water and fire water is centrally supplied. The fire pipeline has a DN250 diameter. There are 14 fire hydrants in the whole plant. The fire pipeline shall be laid according to the requirements of the fire authority and pass acceptance.

### 5.1.4 Air supply

Air shall be supplied by the air compressors located in the other workshops and transferred to the foaming area via pipeline to be used for startup of foaming die.

**The basic requirements of Minea Electrical Appliance Co., Ltd can meet the requirements of the demonstrated project phasing out HCFC-141b.**

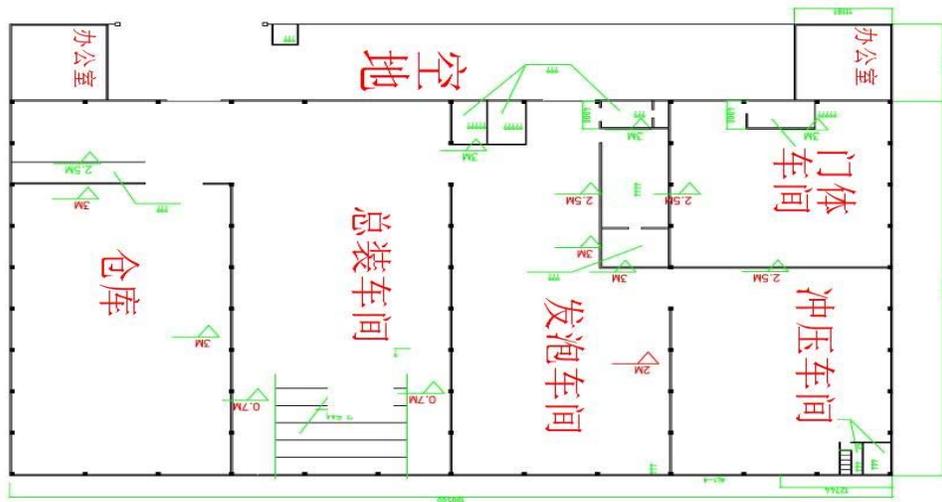
## **5.2 Implementation scheme for formulated polyols with premixed cyclopentane production transformation of Minea Electrical Appliance Co., Ltd**

Minea Electrical Appliance Co., Ltd shall transform the production equipment and auxiliary facility according to foaming technical requirements of cyclopentane.

### 5.2.1 Transformation of production workshop

For this project, 162m<sup>2</sup> partition solid wall needs to be constructed for isolation of foaming working area and the stamping workshop, provided with a formulated polyols with premixed cyclopentane storage room, laid with a ground exhaust air duct in 30m length used for ventilation and exhaust of foaming die during production. It is provided with a cold and hot pipeline in 60m length for cooling and heating the foaming die during production. Some necessary facilities shall be added depending on requirements of exhaust equipment etc. The layout after transformation shall be as follows:

↙ North



## 5.2.2

### Transformation of power supplying facilities

At present, there is one 260 kVA electric power transformer which has sufficient power supplying capacity and can ensure to meet requirements of implementation. For implementation of this project, cable channel and tray shall be installed for the foaming area of foaming workshop and formulated polyols with premixed cyclopentane warehouse, laid with wires and cables, provided with explosion-proof lighting facilities. The existing cold and hot water machines are laid with parallel wires and cables. The electrical switches in the production area shall be transformed for explosion proof.

The project needs to be added with spare supply used for safety detection equipment and exhaust equipment to make sure that the detection and exhaust system can normally run in case of outage or mains failure.

### 5.2.3 Foaming equipment and safety facility

Minea Electrical Appliance Co., Ltd will purchase a unit of cyclopentane high pressure foaming machine and add some safety facilities.

#### 5.2.3.1 Cyclopentane high pressure foaming machine

The physical characteristics of cyclopentane determine that the high pressure foaming machine features very high specificity and technicality, which shall be integrally designed in an open way for purpose of easy maintenance.

A high pressure foaming machine consists of:

a)  $\geq 330L$  jacketed ISO and POL+C5 storage tank. The POL+C5 tank must be provided with safety box made of polycarbonate material anti-static electricity and provided with mixer with magnetic coupling. The ISO storage tank is provided with IP54 mixer, with 5-point safety protection, magnetic color marking liquid level display, and with self-cleaning filter.

b) Provided with variable plunger pump ceramic isolating magnetic coupling

c)  $\geq 10$  inches display, setting and control touch screen, operating system in Chinese interface.

d) Self-cleaning injection gun. The hydraulic oil tank is  $\geq 100L$  and the safety air reservoir  $\geq 10L$ . The hydraulic oil tank is provided with temperature monitor and control and heat exchanger.

e) Gun traveling system.

f) It is provide with 5P water chiller and heat exchanger to regulate and ensure foaming temperature, with 2 safety detector, and with extraction and exhaust air system containing air capacity detection.

Formulated polyols with premixed cyclopentane storage tank is sealed with nitrogen so that the carbon hydrogen foaming agent will not directly be in contact with air (oxygen) for purpose of safety of production. For nitrogen, the nitrogen cylinders shall be purchased from the air separation enterprises.

#### 5.2.3.2 Safety alarm system

Constant emission of gaseous cyclopentane is true. Therefore, it is necessary to provide with monitor and alarm device where possibly emission occurs. Control for production of safety while alarming. The alarm system shall consist of:

a) One unit of control cabinet (the control system is designed with relay)

b) One set of safety control apparatus;

c) Gaseous pentamethylene concentration monitoring system (including 8 detectors);

d) One set of formulated polyols with premixed cyclopentane storage tank drip pan and monitoring device;

- e) Emergency button;
- f) Fire resisting damper;
- g) Fire resisting detector;
- h) Emergency lighting system;
- i) Power supply management (excluding spare power supply)
- j) Door status management (ensuring the door within specified area is NC)
- k) Remote monitor and control (provided in security guard, respectively displaying the alarm status of three control cabinets)

The safety system alarm function mainly includes:

- a) Manual emergency stop alarm
- b) Cyclopentane gas detector and secondary instrument fault alarm. It sends alarm when the CP gas concentration reaches 20%LEL and 40%LEL by stages.
- c) Minimum nitrogen pressure alarm
- d) Air velocity damper alarm of ventilation system
- e) Motor fault alarm of ventilation system
- f) The alarm system can identify fault risk level, controlled by stage. It may effectively control depending on various risk levels. The primary alarm signal sends audible/visual alarm and the secondary alarm signal shuts off the mains and sends audible/visual alarm.

#### 5.2.3.3 Safety Exhaust System

An air duct for the formulated polyols with premixed cyclopentane warehouse extending out roof of the building will be constructed. An air duct for the formulated polyols with premixed cyclopentane storage tank safety box extending out roof of the building will be constructed. An underground air duct is laid in the foaming working area. One air duct extending out roof of the building is constructed on both sides respectively. The fans are provided on the top of the air duct. The fans are one duty and one spare and the air capacity is regulated step by step.

The ventilation system is mainly set up in the high pressure foaming machine and injecting material foaming site. The fans are one duty and one spare and the air capacity is regulated step by step and start step by step depending on CP gas concentration.

Release CP gas concentration to the external environment through the ventilation system and ensure its concentration away from the explosive limit meanwhile.

#### 5.2.3.4 Fire fighting system

The existing plant is provided with concrete pillar with steel structure beam, with color steel roof. For this project, 162m<sup>2</sup> partition solid wall will be constructed for isolation of foaming working area and the stamping workshop as well as one formulated polyols with premixed cyclopentane warehouse. The foaming working area and PPCP warehouse will be transformed as fire resistant Grade II. On the ground and wall of the formulated polyols with premixed cyclopentane warehouse and foaming working area is treated in anti-static electricity and fire proof way. Fire fighting and extinguishing system is provided near the formulated polyols with premixed cyclopentane warehouse and foaming working area and the combustible gas detection and alarm system will be established in the warehouse and foaming working area. It is provided with 3 units of portable fire extinguishers and 15 hand-held fire extinguishers.

Implementation of fire fighting system shall be verified or accepted by the fire authority.

Table 13 Itemization for Safety Facilities of Minea Project

No.	Device	Q'ty	Device to be installed	Remarks
1	Cyclopentane high pressure foaming machine	1	▲ Foaming production line	
2	Gaseous cyclopentane detector	8	▲ High pressure foaming machine (2) ▲ Foaming production line ( 4) ▲ Formulated polyols with premixed cyclopentane warehouse (2)	

3	Air duct	3	<ul style="list-style-type: none"> <li>▲ Formulated polyols with premixed cyclopentane warehouse (1)</li> <li>▲ High pressure foaming machine polyether safety box (1)</li> <li>▲ Foaming working area (1)</li> </ul>	The air duct within foaming area is provided with an underground air duct as well as both air ducts respectively provided both sides underground air duct extending out the roof.
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### 5.3 Specification of Safe Operation for formulated polyols with premixed cyclopentane

The polyurethane foaming production enterprises using formulated polyols with premixed cyclopentane are always small-scale enterprise with weak technical strength. These enterprises cannot meet the safety requirements of pentamethylene foaming only through transformation of hardware. Their personnel need to be trained for safety awareness and safety of production is standardized through improved management system.

Minea needs to improve relevant management system for Minea project phasing out HCFC-141b:

- a) Training and education to staff on safety
- b) Establish management regulations for loading / unloading and storage of formulated polyols with premixed cyclopentane
- c) Cyclopentane foaming production line SOP
- d) Cyclopentane foaming production line safety facilities maintenance and repair SOP
- e) Emergency response plan

## 6 Conclusions

(1) The key technology of premixed cyclopentane and formulated polyols is to solve the compatibility between cyclopentane and polyether; through the sampling investigation of 16

grades' formulated polyols from 6 manufacturers, the results showing that the current domestic polyether suppliers have basically solve the compatibility issue in terms of technology.

(2) Conduct flash point and vapor pressure test on the samples and the results show with the increasing cyclopentane proportion, the hazard of formulated polyols with premixed cyclopentane significantly enhances, proposing higher demand on security measures in the production application process.

(3) Formulated polyols with premixed cyclopentane is Class II flammable liquid according to relevant national regulations.

(4) According to the safety assessment, the demonstration project is proposed to add the relevant security facilities shown in table -12. The conversion plan of Wanhua Rongwei is in line with the relevant safety standards and codes, being able to prevent and control various conditions in production process.

(5) Formulated polyols with premixed cyclopentane may safely be transported in a short and medium distance when strictly following relevant regulations of dangerous chemicals transportation.

(6) The conversion plan of Minea Electrical Appliance Co., Ltd will meet the requirements of cyclopentane foaming. However, trainings shall be conducted to the personnel to raise awareness on safety and help them handling the materials properly. The management system concerning safety production shall be strengthened.

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