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A Case Study of Cleaner Production in Acrylonitrile Butadiene Styrene Resin Companies in China

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Abstract: This study aimed at helping an Acrylonitrile Butadiene Styrene (ABS) resin company to improve its environmental performance and comply with the sustainable development required by Chinese government and corporation itself. The processes of ABS resin production amounts of waste gas, water and solid waste. In the most cases in China, the environmental issues from this industry have been focused on the end of pipe treatments during the last two decades. Recently, with the increasing emphasis on environmental protection from the society and the needs of enterprise self-development, the cleaner production programs have been introduced in some ABS resin companies. In this study, we made a close examination of ABS resin company in Ninigbo, an important light industry base in Eastern China. Base on understanding of ABS resin processes and collecting data of energy consumption, resource consumption and discharged pollutants, cleaner production opportunities for three main steps of ABS processes were analyzed. Cleaner production options were proposed for emulsion grafting process step. The feasibility studies for 4 higher-cost options were delineated in this study. After implementing 30 different independent cleaner production options, the company improved its environmental performance obviously. Material consumption and energy consumption per unit product decreased 10.05 and 15.5 kg tce, respectively. Cleaner production brings remarkable economic and environmental benefits for the company by means of energy saving and pollution reducing.

Key words: ABS resin, cleaner production, options, energy saving, pollution reducing

INTRODUCTION

The amount of natural resources, including energy, per capita in China is poorer in the world and the Chinese industry production is at lower level compared with the developed countries currently. Meanwhile, with extremely rapid economic development the environment issues become the key element to restrict industries developing. Since, Chinese government promised to adapt the principle of sustainable development to take environmental responsibility in 1992, the industrial sections have been improved their environmental performance a lot according to Chinese policy. In 1993, the central government addressed the pollution control on the cleaner production. In 1996, it has been cleared that all large, medium

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and small construction, expansion, reconstruction and technological transformation projects should take cleaner production into consideration for saving energy and minimizing material consumption, improving production technological and processes control, reducing pollutants discharging. In 2003, The People's Republic of China Cleaner Production Promotion Law formally launched. Since then, the industrial are more and more interested in cleaner production instead of end-of-pipe treatment. Until now the Cleaner Production Auditing (CPA) projects have been implemented countrywide. Various industries are involved in the CPA projects, such as chemical, light industry, building materials, metallurgy, petrochemical, electric power, aircraft manufacturing, pharmaceutical, mining, electronics, tobacco, machinery, textile printing and dyeing, as well as transportation and other industries (China National Cleaner Production Center, 2007). Cleaner production brings both economic benefit and environmental benefit for industries. Industries are gradually realizing the cleaner production is the way to help their business from the sustainable development point of view.

Ningbo is located in the East China Sea coast of South-East corner of the Yangtze River Delta. With over 100 years development, it has become a country and an important energy, raw materials base and export processing zones, the Yangtze River Delta and Yangtze River, an important chemical industry bases in coastal areas and foreign trade port. It is also a center for economic development in Zhejiang Province even in China. The economic status is very important. During the industrialization more than 30 years, Ningbo has been basically formed a stretching over 20 km of the coastal port industrial zone. The petrochemical industry has become an important industrial sector in the region. Polypropylene resins, propylene oxide, polyether polyols, propylene glycol, Acrylonitrile Butadiene Styrene (ABS) and others are the main products of the region's petrochemical industry (Ningbo Municipal Development Planning Commission, 2006).

ABS resin is Acrylonitrile (A), Butadiene (B) and Styrene (S) from three monomer copolymer thermoplastic polymers. Styrene introduces the resin rigidity, electrical properties, easy processability and surface gloss, butadiene makes the resin low temperature impact toughness and acrylonitrile confers the resin chemical resistance, weatherability, heat resistance and tensile strength. As the three-component combination is of complementary advantages, all of these characteristics make the ABS resin show excellent performance (Li and Wu, 2006a,b), such as heat resistance, surface hardness, dimensional stability, chemical resistance and good electrical properties, ease of molding and machining. Therefore, the ABS resins have been used widely in electronic and electrical appliances, instrumentation, automotive, building materials industries and daily-use products.

The consumption patterns of ABS resin are very different in all parts of the world. In western European countries, ABS resin is used mainly in automobile, appliance and telecommunications fields. In addition to these fields, in Northern America, it has been used in construction (pipe) areas. In Japan and Korea, the resin is mainly used in the automobile industrial sector. In other countries of Asia-Pacific region, ABS resin is mainly used for producing appliance, telecommunications and toy. In China, the ABS products are widely used in electronics, light industry, building materials, automobile and other fields. Among these, about 80% of ABS resin is used electronics field (Suo *et al.*, 2004).

Research and development ABS resin products began in 1960’s in China. At Lanzhou Petrochemical Company, with the synthetic rubber emulsion grafting, the first set of the ABS resin production line was completed in 1975. The production capacity was 2,000 tons year^{-1}. A chemical plant of gaoqiao petrochemical company established another ABS resin production line in 1978 in Shanghai. The process called graft emulsion-emulsion admixture process was developed by the plant itself. But, until early 1980's, the development of ABS resin production was very slow. Resin productivity could not meet the rapidly need of the domestic market. The most part of the ABS resin used in China were imported from abroad (Li and Li, 2006).

China is the largest consumer of ABS resin in the world. Due to rapid development of household appliances and automobile industry, ABS consumption has been growing rapidly in China since the 1980's. In 2000, the apparent consumption of ABS resin was about 1,766,000 tons. The number increased to 2,989,000 tons in 2005 and in 2006 it reached to 3,274,000 tons. It is expected the demand in 2010 will reach 3.82 million tons. Meanwhile, self-sufficiency rate of ABS resin in China was only 18.35% in 2000. In recent years, as China's ABS resin production capacity and output are growing, self-sufficiency rate of ABS resin in China has reached of 34% in 2005 (Lin *et al*., 2007). In 2006, the production of ABS resin was 1,390,000 tons in China and it is expected that production capacity will reach about 3.4 million tons until 2010. There is a large gap with the demand in 2010 (Xiang and Xiao, 2005).

In order to meet the demand of the market, a number of domestic enterprises have come into production or increasing productions (Suo *et al*., 2004; Lin *et al*., 2007) during the last decade. At present, the most productions of ABS resin are from LG Chongxing Co. Ltd. in Ningbo, Chi Mei Corporation in Zhenjiang, Petrochemical Company in Jilin, Zhenjiang Guoheng Company, Xinhu petrochemical company in Changzhou, etc. In addition, Sinochem Corporation, Gaoqiao Petrochemical Company and BASF Company in Huizhou have also been put into operations (Xu and Han, 2006).

In the process of ABS resin, there are a large amount of exhaust gas, wastewater and solid wastes. For the pollution control, the most options applied were focused on the end-of-pipe treatment mainly. In the developed countries, cleaner production options have be introduced into the ABS resin process. In these cases, the attempts were focused on the improvements in process and technical (Brebu *et al*., 2005; Miskolczi *et al*., 2008). With the increasing emphasis on the enterprise responsibility to the environmental protection and to meet the need of the enterprise self-development, a lot of ABS resin production enterprises have been carried out cleaner production actively in China (Xu, 2006; Zheng, 2007; Pan *et al*., 2005). In present study, a case of cleaner production in ABS resin production in Ningbo was introduced. In this case, with the understandings of the process, energy and resource consumption, pollutants generation, treatment and discharge, the significant environmental problems of enterprises were identified. For solving these problems, cleaner production options were suggested. The options include a comprehensive energy use, the reform process and equipment, materials recycling, good-house keeping improvement, product substitution and the development. After implementing these options, pollution controls, material and energy recovery has been strengthened. It resulted in obvious environmental and economic benefits. The case gave the ABS resin enterprises a good sample with valuable ideas, environmental performance improvement and economic benefits of cleaner production implementation in China.

PROCESS OF ABS RESIN

Until now, the techniques for the ABS resin production can be classified into 3 groups, which are chemical grafting, chemical grafting blending and physical mixing. In the chemical grafting blending, it can be divided into the emulsion grafting-SAN latex (Acrylonitrile-styrene copolymer resin) blending, the emulsion grafting-SAN suspension mixing and the emulsion grafting-bulk SAN blending. The last one is a mainly production

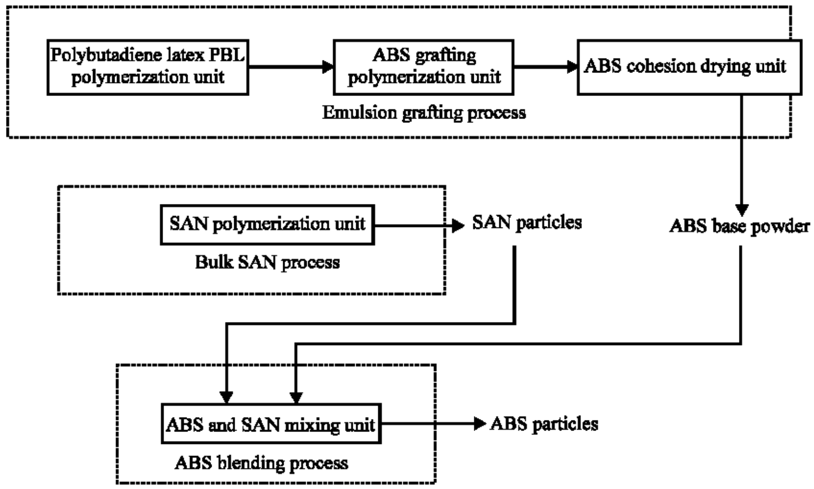

Fig. 1: The flow diagram of production steps

method in ABS resin production in all parts of the world as well in the case of the polypropylene company, we mentioned here. The company has an ABS resin productivity of 250,000 tons year^{-1} (Li and Wu, 2006a,b).

The emulsion grafting-bulk SAN latex blending process is developed mainly at the basis of the emulsion grafting. The process is complex and included in the synthesis of trunk latex used for grafting, the graft copolymerization of the trunk latex, styrene and acrylonitrile, the synthesis of bulk SAN copolymer and the mixing of ABS grafting copolymer with SAN. Figure 1 shows these steps in a flow diagram of the company's production.

THE CONSUMPTIONS AND EMISSION BEFORE THE CLEANER PRODUCTION

The main raw materials in the company are styrene, acrylonitrile and butadiene. Water is used mainly for the production. The main energies used are electricity, steam and heavy oil. During the production, the major environmental impacts are resulting from the process gas emission, wastewater and solid wastes.

The Consumptions of Raw Materials, Water and Energies

In 2006, the unit consumptions for the ABS resin production were styrene 645.99 kg ton^{-1}, acrylonitrile 223.80 kg ton^{-1}, butadiene 144.64 kg ton^{-1} and auxiliary materials 39.62 kg ton^{-1}, respectively.

The consumption of water was mainly for the process in the company. The consumption of fuel oil was used for operating heating kerosene boilers. The electricity consumptions was used for the extruders, air compressors, ammonia freezers, ammonia compressors and all kinds of pumps for cooling water cycling and oil cycling. The steam consumptions were for the heating and keeping warm during the process. Table 1 shows the data of unit consumptions of water and energies in 2006.

Generation and Emission of Pollutants

Process Wastewater

The process wastewater were discharged from different processes, including wastewater from the dehydration of ABS grafting base materials, waste cooling water from the ABS resin

Table 1: Consumptions of water and energies

Items	Water (m^3 ton^{-1})	Electricity (kWh ton^{-1})	Steam (t ton^{-1})	Heavy oil (kg ton^{-1})
Consumption	5.99	823.80	0.44	27.65

extruders, wastewater from the cycling system and the palletizing of SAN reactions, washing wastewater from the waste process gas scrubber used for dryers of ABS grafting base materials, waste cooling water from ABS emulsion reaction tanks, wastewater from the scrubbers for the gases in the process of the ABS reaction, cohesion, settle and feed. A total amount of process wastewater in 2006 was 1,528 m^3 per day.

In the company, there is a wastewater treatment plant with a treatment capacity of 6,000 m^3 day^{-1}. In the plant, after primary treatment of buffering, balancing, neutralization, flocculation, flotation and secondary treatment of biochemical and grit filtration, the secondary class national wastewater discharge standards were met.

Process Gases

The process gases from the ABS production were composed of styrene (SM), acrylonitrile (AN), Butadiene (BD), sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and dust (TSP). Among of them, SM, AN and BD were from ABS process, SO_2, NO_2 and TSP were from the burnings of direct combustion incinerators, regenerative incinerators and heat medium heater.

The process gases that are emitted regularly can been divided two groups based on the pollutant concentrations in the gases. The process gas with high pollutants concentration was treated by the direct-fired incinerators and the low pollutants concentration one was treated by the Regenerative Thermal Oxidizer (RTO). In emergency, abnormal exhaust was dealt with the ground burning tower.

The high concentration gases derived from the ABS emulsion reaction tanks, cohesion tanks, settle tanks, dehydration and charge tanks and as well dehydrators, breathing exhaust of SM, AN storage tanks and ABS extruders.

The low concentration gases were emitted from the inertia collectors in dryer for ABS grafting base materials and washing towers, SAN recycling system, dies of SAN granulators, wastewater collection tanks and sediment tanks, ventilation cabinets in the lab. and a heat medium heater.

The gases which emitted irregularly during the ABS production were breathing emission from storage tank for volatile materials, granulators and extruders, gas leaked from pump seals, valves and tube connectors and the gas from lab ventilation and from wastewater collection tanks.

Solid Wastes

Solid wastes were mainly from the sewage treatment plant and the production devices. The solid wastes were composed primarily of biochemical sludge and the variety of polymers. Enterprises set up an incinerator burning them or transferred to local qualified solid waste treatment stations to deposit and disposal.

The amounts of pollutants discharge in the company were listed in Table 2. Because, many options complied with the cleaner production requirements have been used in design, construction and process management and the better pollution control facilities have been equipped with, so that the pollutants discharge of unit production were relatively lower.

Cleaner Production Statuses

In terms of saving energy, the company has been taken it into its consideration since the design. The company equipped with large mounts of the efficient motors with controlled

Table 2: Pollutants discharge of unit production

Pollutant	Discharge mount
Wastewater (m^3 ton^{-1})	4.288
Discharge of main pollutants in wastewater (kg ton^{-1})	
COD	0.357
NH_3-N	0.0583
Waste gas (m^3 ton^{-1})	7368
Emission of main pollutants in the gas (kg ton^{-1})	
SO_2	0.347
Dust	0.202
Solid waste (kg ton^{-1})	27.26

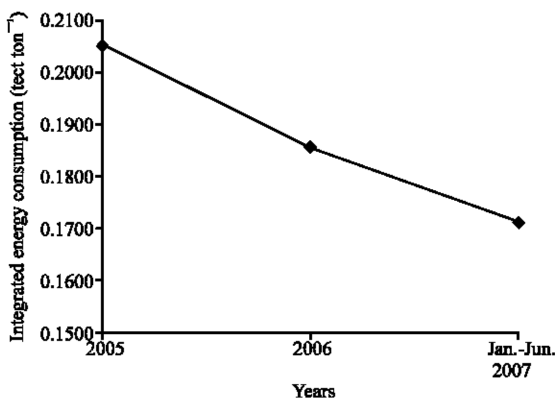

Fig. 2: The decrease of integrated energy consumption in the company (tce ton^{-1})

by the inverters during the construction. It resulted in reducing of electricity consumption from very beginning. The use of low-voltage capacitor plate made the electric virtual work to a minimum and efficient. Now the power factor in the company arranged from 0.96 to 0.98. Meanwhile, the large size equipments were controlled by the computers. It was good to automatically adjust the equipments that resulted in a stable and efficient operation. By carrying out these options, during 2005 to 2007, the integrated energy consumptions have been decreased from 0.2051 to 0.1716 tce ton^{-1}. The decreasing reached 16.33% (Fig. 2).

In terms of material consumptions, the enterprise applied many options which resulted in to reduce the anomaly, keep the stable production and maintain a lower material consumption. For example, in SAN workshop, recycling and reusing the unreacted monomer, recycling the raw materials, exhausted by the vacuum, with extraction column, filtered water recycling after the delivery from the granulators, settings filter bag to filter material and to reduce wear and tear, pollution on the air transportation system. In BP workshop, wet scrubbers have been installed in the dryers, at the top dryers the fine dust were collected by a cyclone collector system. After these options, the material consumptions of the ABS particles in the company have been decreased from 1,064.21 kg ton^{-1} in 2005 to 1,049.84 kg ton^{-1} (Fig. 3).

In terms of reducing pollution, except the whole process control of the pollutions, the treatment systems for the process gases, waste liquids and wastewater have been constructed as well. In the area, from where the gas could disperse like wastewater collection tanks and raw material storage tanks, some lids and pipes were used. It decreased the irregular emission of the gas effectively. The low sulfur heavy oil, sulfur concentration is lower that 0.39%, used as the fuel oil in the company. The heat medium heaters were equipped with spray gun combusting low-NO_x heavy oil so that the emissions of No_x and

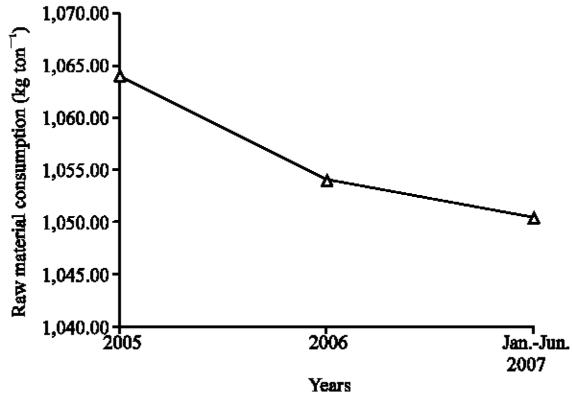

Fig. 3: Raw material consumptions in ABS process (kg ton^{-1})

So_x were decreased. The non-spindle sealed pumps were used for the transfer of the raw materials in the process in order to reduce the possibility of pollution leakages from spindle sealed pump.

Cleaner Production Options

After the analysis of the energy consumption, material consumption, pollutants and emissions in the process, 41 cleaner production options and the rationalization proposals have been suggested by managers, workers, technicians, experts and consultants. They were focused on 8 different fields, including the use of raw and auxiliary materials, process technology improvements, equipment maintain, process control optimization, operation management, waste recycling, personnel training etc. Among these, workable options proposals were 38. The investment was estimated of about 21.87 million Yuan. In these options, there were 4 medium/high cost options, accounting for 13.2% of the total program and 33 no-cost/low cost proposals, accounting for 86.8%.

In this study, feasibility studies on these 4 medium/high cost options were described as follows:

Removal Dimethylformamide (DMF) from the Waste SAN Resin after Washing

A new waste liquid tank has been installed in the wash machine to collect DMF contained waste resin into the tank. The tank was kept warm by the heat media oil to prevent the resin solidification. The remained DMF was extracted from the waste liquid with a water-sealed vacuum pump. The DMF-removed waste resin was let out into the waste resin recycling bins for sale. This black material can be used by the downstream manufacturers to produce low quality resin. The DMF steam from waste liquid was condensed with a shell and tube heat exchanger. And then, the condensed DMF, recycled into a storage tank, can be reused in a new wash process. The cleaner production option cost 600,000 Yuan. After implementing the option, it was estimated that about 160 tons year^{-1} solvent are saved due to recoverable DMF and about 150 tons year^{-1} waste resins can be recycled for the downstream firms. About 320 tons wastes and 32 tons fuel oil was reduced each year. The economic benefit of 3 million Yuan year^{-1} was gained.

Transducers in the Dehydrators for the Base Powder Dry

In this process, the new transducers were added in for reducing the startup current and protect the motors. By means of transducers production speed could be regulated automatically for keeping the stability of the production, saving energy and protecting environment from pollutant discharge during abnormal shutdown. The option cost about 1 million Yuan and save running cost about 600,000 Yuan year^{-1}.

Improvement of Transfer System of BP Base Powder

The bag filters were installed to suck the gases, emitted from the oscillating screens and rotary valves and the larger diameter gas pipes were used to improve the effect of exhaust. In order to tone up rotary valve gastightness, the gap of between the rotary valve rotor and the shell was adjusted from 0.25 to 0.21 mm. It resulted in lessening the escape of the compressed air, which cause the loss of the powder-based material from oscillating screens. This option cost 150,000 Yuan and result in off-grade products reduced from 150 to 40 tons year^{-1} and reduce 30 kg drifting lost of the base powders per day. The benefit reached 500,000 Yuan year^{-1}.

Improvement of the Oscillating Screens

A new type oscillating screen has been used in the options. The mesh diameter of upper screen of the new oscillating screen was changed from 6.0 to 5.5 mm. The thicknesses on the upper and lower floors were changed from 2.0 to 0.8 mm. The punching clearance on the upper is 7 mm and on the lower is 3 mm compared with original 8 and 4 mm, respectively, so, that the through-hole rates in the upper and the lower have been increased to 15 and 20% respectively. The 60° cross angle was designed to eliminate the blind spots. The option improved oscillating screen performances. The improvements resulted in to solve overflowing of normal particles due to the over size particles walled up the mesh. With 700,000 Yuan investment, the off-grade products have been reduced by 50% and the obtained benefit was 127,500 Yuan year^{-1}. It showed that the rate of finished SN products increased and raw materials consumption decreased.

IMPLEMENTING EFFECTS

After implementation 30 cleaner production options, included 3 medium/higher options, the obvious economic and environmental benefits have been achieved, for examples, unreacted BD in BP reaction tanks was reused by the recycling system, which transported unreacted BD back to the reaction tanks. It saves 220 t BD and 2,116,400 Yuan raw material cost year^{-1}. Meanwhile, the process gas emission has been reduced.

With the introduction of new technology invented by parent company, the product of BP 818 is replaced by BP 828. Under the certain ABS productivity, it could reduce 3600 tons of the ABS base powder production and the indirect benefit is 2 million Yuan year^{-1}.

By adjusting the operation time of cooling water recycling pumps in PBD latex tanks, the operations time reduced from 26 to 1.5 h. It could save electric power 860,000 kWh per year and save electricity fee 3,780,000 Yuan RMB.

In addition to the improvement of the oscillating screens, there were 3 medium/higher cleaner production options have been adopted in company. A total cost is 1.707 million Yuan RMB. A 3.696 million Yuan RMB benefit has been got. The significant economic and environmental benefits have been made.

With the cleaner production programs, the material consumption of unit production of ABS and BP base powder is reduced 10.05 and 4 kg, respectively, energy consumption of unit production of ABS decreased 5% with reducing of 15.5 kg tec. The cleaner production in the company has reached to the advance level in the world.

DISCUSSION

As an important chemical raw material product, ABS has been used broadly in many aspects of human life. It is similar to other chemical products that a variety of hazardous substances is generated to environment in the ABS production process (Zhao *et al*., 2003; Chen *et al*., 2007). From the references and formal documents, we knew that the corporation CPA is not only implemented by the EU and the Chinese government, but also needed by corporations for their environmental performance and linked with their own contributions to the socialites (EUC, 2003a, b, 2005; The Standing Committee of the National People's Congress (NPC) of the People's Republic of China, 2003). By the CPA, the potential environmental hazards from processing could be found and the potential problems on the resource utilization, energy consumption and cost accounting and the others as well (Hillary and Thorsen, 1999; Gale, 2005; Holton *et al*., 2010). The CPA is not the goal of complying environmental regulation. By means of CPA, identifying the problems, proposing the solution options, implementing the options in line with the characteristics and requirements of production, keeping scientific management and technical measures could be done by all the firms. It is enable to help enterprise maintain a healthy development trend, meanwhile to be accepted by the society as the environmental friendly company both in economic and ecologic field.

There is no CPA report on the same ABS process plant, although some ABS plant have been innovated their production facilities to reduce water use and wastewater pollutants discharge. Till now, there are more than 20 industrial standards on cleaner production and more than 20 cleaner production index systems for different industry section issued in Chinese, but non of them is about ABS production. In this case, the enterprise has achieved very good results on both environmental benefit and economic benefit on resource use and energy consumption through the implementation of the cleaner production options. The similar results have been achieved in the chemical industry of China with many cases (Liu and Zhang, 2004; Yang, 2009; Ling, 2008; Tang *et al*., 2009).

CONCLUSIONS AND RECOMMENDATION

Although, many advanced production techniques have been adopted in the enterprise involved in this case and cleaner production opportunities have been excavated from intra-enterprise since, setting up the company. Many cleaner production options have been designed and implemented from the views of energy use, process and equipment reform, materials recycling, production management, product substitution and development during cleaner production auditing procedures.

After implementing the options, the consumptions of materials and energy in the process have been reduced in further and the discharge of pollutants has been decreased as well. The purpose of energy saving, material consumption decreasing, pollution reducing and efficiency increasing has been achieved. The cleaner production of the enterprises has reached up to world's advanced levels.

Cleaner Production is an ongoing work, so that it is recommended to establish a complete incentive mechanism to improve the cleaner production regularly and to constantly promote decreasing the energy and material consumption and reducing pollution emission, to deduct production costs and to strengthen company's market competitiveness. Some suggestions are as follows:

The company should improve the consumption assessment and management system for each process step as soon as possible and to implement the assessment. The energy indicators for assessing the different machines and the different departments should be researched more to be sure that they are reasonable. Energy consumption ratio of different steps and products should be identified in detail. A strict rule of awarding for energy and material saving and penalty for overusing should be set up. It could explore enterprises in good house keeping, equipment operation, process control for energy-saving potential, to achieve energy saving and cost reduction purposes.

The company should strengthen its measurement and monitoring for the wastewater and process gas control facilities, to protect the normal operation of the environmental protection facilities and to eliminate abnormal emissions.

In the enterprise, the zero emissions should be considered as a concept, not only to vigorously implement the water saving options, but also to use the new wastewater treatment techniques. It would promote the water reuse, reduce the wastewater discharge and conserve water resources.

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