ing in earthenware and aging. The steps are similar to those used in making bean curd, with some important differences.

Addition of coagulant. An inorganic salt, such as calcium sulfate, is inappropriate for making fu ru. The coagulant used is derived from the mother liquor which is pressed out of the bean curd. The liquor sets for 2 days until the pH reaches 4. This coagulant shortens the time of natural fermentation for the bean curd.

Ten min after the coagulant is added, the soy milk coagulates. It is then wrapped and pressed. The liquid should be pressed out as much as possible to prevent the accumulation of too much water which will affect the growth of the filamentous fungi. Then the pressed curd is cut into small pieces. The total solid content should be 35%.

Fermentation. The pieces of bean curd are arranged on wooden frames and put into the fermentation room at 18-20 C. Natural fermentation follows for 3-4 days. The hyphae of filamentous fungi grow to ca. 10 mm thickness on the surface of bean curd.

Salting. After fermentation, the bean curd is salted by arranging them in the large vats and spreading every layer with table salt. One day later, the hyphae will have adhered to the surface of the bean curd. Salt water (ca. 18 Be') is then added. The salting period lasts for 10 days.

Packing in earthenware. The fermented bean curd pieces are transferred to a small earthenware jar and spices are added. The pieces of bean curd are soaked in the spicy liquid. The spices usually are Chinese prickly ash seed, anise and red pepper. Red fu ru is prepared by adding Red Koji (a fermentation product used as coloring matter in food) as a tint to make the fu ru a crimson color and give it a different flavor. There are 10 or more varieties of this fu ru on the market.

Aging. The small earthenware jars filled with fu ru are placed in a room to age at 30 C. The aging period is generally 6 months.

Dried Bean Milk Cream (Fu Tsu)

When the soy milk is heated in a shallow pan, a film consisting of oil and protein is formed on the surface. This film is rolled out and dried until it resembles a cut of bamboo, hence the name "Fu tsu." Its composition is similar to textured vegetable protein. The procedure includes soaking, grinding, separating from the residue, boiling, skimming and drying. The initial preparation is like that of the soybean milk already described.

Skimming. The concentration of the soy milk should be ca. 7 Be'. The boiled soy milk is poured into shallow pans (3 m x 0.6 m x 0.1 m) which are divided by wooden plates into 10 equal parts. The pans are heated by indirect steam. The temperature of the bean milk is maintained at 90-95 C. The surface film is skimmed, rolled out and hung over a rod. The thickness of this film is ca. 0.15 mm. The percentage yield of fu tsu is ca. 60% of the original soybean.

Drying. The wet fu tsu is dried at 50 C in the drying room. After 24 hr the moisture content drops to below 10%.

Soybean protein products are among the favorite foods of the Chinese. In addition, vegetarians or those who suffer from hypertension need these products for good nutrition. Even though some new products, such as soybean milk powder and texturized soy flour, are being marketed, the demand for traditional protein products is increasing.

A Review of the Detergent Industry in China

HONG-XIN TANG, Detergent Division,
Research Institute of Daily Chemical Industry,
Ministry of Light Industry, Beijing,
The People's Republic of China

ABSTRACT

This paper is a general review of the development of the detergent industry in China. Examples include alkylation with aluminum ingot, dehydrogenation catalysts, double-film SO_3 sulfonator and enzymatic detergent.

In China, cleaning materials were available centuries ago. Some of these were straw ash, soap pod, teaseed cake and alkali-blended pig pancreas. The modern soap industry began in 1903 and soap is still the main laundry product in this country. The synthetic detergent industry, which started in the late 1950s, has developed rapidly. In 1979, the production of soap and detergent was rated at 734,000 and 397,000 tons, respectively, indicating a low level of consumption per capita (ca. 1.3 kg), compared to the developed countries. The annual production for the past two decades of soap and detergent is shown in Figure 1. In general, the annual increase is ca. 10%. The production of soap in 1977 was estimated to be 8 times higher than that in 1949. Production of detergents has risen from 6% of total cleansing products in 1964 to 35.8% in 1978. Greater expansion in the detergent industry is expected in the future.

China's soap-making technology is conventional. It induces a cooling process for laundry soaps and a milling process for toilet soaps. There are laundry soaps containing 53, 56, 65 and 72% fatty acids. Toilet soaps contain more than 78.5% of fatty acids. Laundry soaps total 90% of soap production.

Among detergents, the powdered products are predominant, making up 95% of the total. There are several grades of detergent powder on the market containing 20, 25 and 30% of active material. Paste-type detergent is estimated at 10,000 tons. In addition, liquid and cake products are also available. In China, home laundering is done mostly by hand. Washing machines are not very common in households, although they are popular in laundries, hospitals and hotels.

Also available is a wide variety of surface-active agents in which linear alkyl benzene (LAB) is the predominant ingredient. Two processes are used to produce LAB. In the first, the normal paraffins from the molecular sieve or urea extraction are subjected to chlorination, and benzene is then alkylated with the chlorinated paraffin to produce LAB. In the second process, paraffin wax is thermally cracked to olefins of different molecular weights, a fraction of which is reacted with benzene to produce LAB. The production capacity of both processes is nearly equal. The total production of LAB was 37,700 tons in 1979. A new alkylate plant (UOP process) with a capacity of 50,000 tons/year was scheduled for start-up in 1980.

A higher paraffin fraction (C_{15}-C_{18}) from urea extrac-

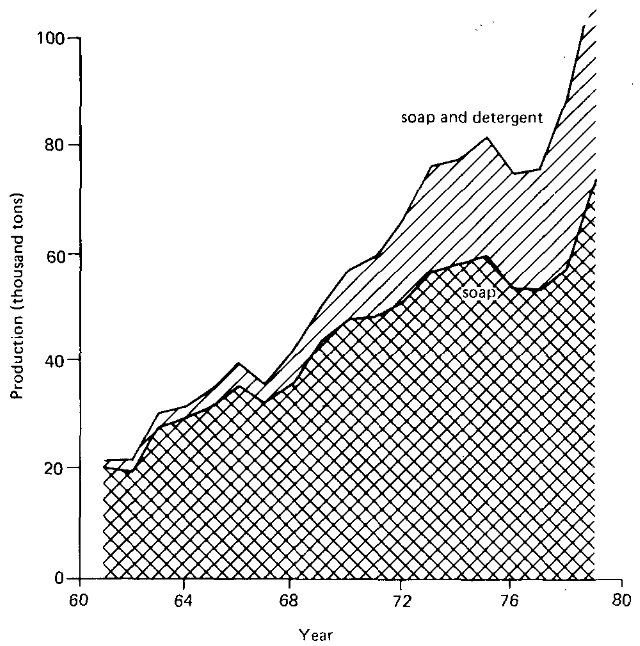


FIG. 1.

tion is reacted with sulfur dioxide and chlorine to give alkyl sulfonate as an industrial surface-active agent.

Since 1961, paraffin wax has been used in liquid phase oxidation to obtain synthetic fatty acids for soap-making as a substitute for edible fats and oils. The annual production of C_{10}-C_{20} acids was 57,800 tons in 1979. Both natural and synthetic fatty acids are esterified and hydrogenated in the presence of a heterogeneous catalyst to fatty alcohols which are used as a raw material for synthetic detergents, foaming agents and nonionics.

We also have a variety of nonionic surface active agents, such as ethylene oxide condensates of fatty alcohols, alkyl phenols, fatty acids and fatty amines as well as alkylolamides, but they are produced in smaller scale, making up less than 10% of the total active materials. Nonionics are used mainly in industries. Some quaternary cationics and amphoterics are produced in small quantities.

As for detergent builders, tripolyphosphate is produced mainly using the wet process. As the present supply does not meet demands, a larger, hot process plant (Udhe Co.) with a capacity of 110,000 tons is now under construction. Other builders, such as carboxymethylcellolose sodium salt and optical brightening agents, also are available.

Oleum is widely used as the sulfonating agent in the dominant bath-type process for alkylate sulfonation. Some plants use sulfur as a raw material to produce sulfur trioxide as a sulfonating agent. The detergent beads are made by continuous spray-drying whereas slurry preparations are done in batches.

Paper and plastic film are used as the package materials for detergent powders. Paper packaging machines for powders and film packaging machines for pastes are used in some plants, but in others, packaging is still done by hand.

In China, the quality of the water supply is extremely diverse. For example, the water hardness is ca. 80-90 ppm in Shanghai and Kwangchow, whereas it is up to 400 ppm in Beijing, In many districts, water hardness is above 250 ppm. Most laundering is with cotton fabrics, but the proportion of polyesters and nylons has been increasing steadily. Under these conditions, a higher active material formulation is preferred for hand-washing. Typical powder formulations are listed in Table I. There is no product with an oxidizing agent like sodium perborate. Some powdered products with an enzymatic ingredient are available on the market.

In brief, an increasing trend toward a steady growth of linear alkylate production is expected, while the use of detergent fatty alcohols will increase even faster. The heavier fractions such as C_{14}-C_{18} normal paraffins from petroleum will be considered as new raw material for detergents. Water pollution from tripolyphosphate is not considered serious in China because of its relatively small use; hence, polyphosphate will be developed further. In order to meet the ever increasing demand for detergents, we have to enlarge the supply of raw materials and adopt advanced technologies. New products must be developed to satisfy household and industrial needs. Research institutes, specializing in the field, are tackling this problem. Some are afflicted with factories. Examples of research and development follow.

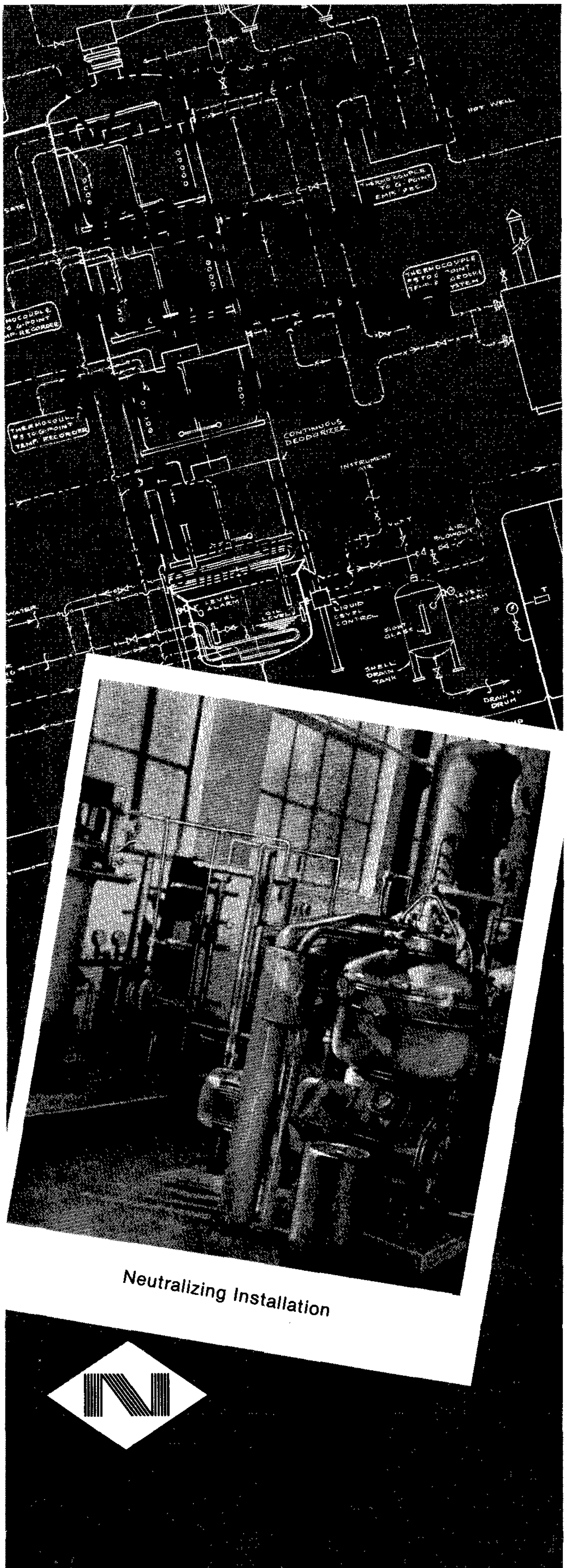
Alkylate is prepared by the alkylation of benzene with chlorinated paraffin in the presence of $AlCl_3$. Usually, aluminum powder or granules are used to control the amount of the catalyst. A process has been developed for the direct use of Al ingots in which Al blocks, cut from ingots, are put into an Al-dissolving tower and charged once every few days. The slurry from the settling tank is pumped to the Al-dissolving tower, thus dissolving the Al with the formation of $AlCl_3$, which is then sent to the alkylation system. The amount of Al dissolved is dependent on the amount of HCl brought into the tower by the slurry. Under normal conditions, the amount of HCl carried over by the slurry is constant. The amount of Al in the alkylation system is increased accordingly with the increase of the slurry sent to the Al-dissolving tower. It is easy and convenient to adjust and control the amount of $AlCl_3$, thus producing a smooth reaction and a product of good

TABLE I

Detergent Powder Formulations

Ingredients	30 AM[a]		25% AM	20% AM
Linear alkyl benzene sulfonate	30	30	25	20
Tripolyphosphate	30	16	12-16	12
Water glass	4.5-7	5-7	5-8	8
Soda	0-2	0-3	4-6	10
Carboxymethylcellolose	1-2	1-2	1	1
Brightners	0.1	0.1	0.05-0.1	0.05-0.1
Sodium sulfate and water	balance	balance	balance	balance

[a]AM = active material.



quality and high yield.

Complete data concerning the vapor pressures of the normal alkyl benzene isomers are not available. We have deduced the vapor pressures of different isomers of C_9-C_{15} linear alkyl benzenes from the calibrated retention times of isomers of C_{11}-C_{14} linear alkyl benzenes.

In studying chlorination alkylate, we separated, using an adsorption column, monoalkylbenzenes, dialkylbenzenes, indanes and polyphenyl paraffins. The physical properties and the sulfonation behavior of these substances, as well as their sodium salts after sulfonation, have been investigated separately, and hence we have obtained information to improve this process.

A new catalyst for the dehydrogenation of C_{10}-C_{13} normal paraffins has been developed. The carrier used is γ-Al_2O_3 with bidispersed pore structure. A special method is used to prepare the catalyst from this carrier. A pilot plant has been built to test the performance of the catalyst with an adiabatic reactor of 1-ℓ capacity. A mixture of olefin and paraffin from the reactor is reacted with benzene in the presence of HF and the unreacted paraffin is recovered from a distillation column. After deflorination, the paraffin is re-used. After 2 months' operation, the temperature of the catalyst bed is raised by only 6 C, which gives stability to the catalyst. The product distribution indicates good selectivity of the catalyst.

In the investigation of sulfonation, a double film sulfonator, with the reaction taking place in annular space, has been produced. The main problem is the uniform liquid distribution. A special box-type distributor has been designed and used on a commercial scale. The distributor is a concentric, circular box and the granules of inert substance of uniform size are put into it. Alkyl benzene, passing through the box, is distributed along the periphery to give a uniform liquid film. In practice, the box gives very good results even without the filler. The box structure is rigid, holds its shape and is easy to set up. The SO_3 gas and protective air are led through multiple tubes to secure uniform gas distribution. This kind of sulfonator gives products of good quality.

In the manufacture of enzyme detergents, the conventional procedure is to mix the enzyme powder into a detergent product. We have attempted a direct adhering process. The refined enzyme solution adheres to the detergent beads in a fluidized bed with a nonionic adhering agent. The proportion of enzyme liquid is small, and if the enzyme solution is well purified, the whiteness of the detergent bead is not impaired. There is no substantial change in bulk density, water content or particle size. This produces a good quality enzyme detergent. It should be possible to eliminate the procedure of making enzyme powder resulting in a safer process.