DRYING OILS—In this symposium are *(seated)* H. J. Lanson, General Electric Company, Schenectady, N. Y.; R. W. Tess, Shell Development Company, Emeryville, Calif.; M. W. Formo, chairman, Archer-Daniels-Midland Company, Minneapolis; Odin Wilhelmy Jr., Battelle Memorial Institute, Columbus, O.; and J. A. Cannon, Northern Regional Research Laboratory, Peoria, Ill.; *(standing)* E. F. Fitzgerald, E. I. du Pont de Nemours and Company, Philadelphia; C. G. Youngs, National Research Council, Saskatoon, Sask.; R. L. Terrill, Spencer Kellogg and Sons Inc., Buffalo; W. O. Lundberg, Hormel Institute, Austin, Minn.; H. M. Teeter, Northern Regional Research Laboratory, Peoria; and E. W. Eckey, Eckey Research Laboratory, Cincinnati, O.

Emphasize Research, the Key to Future Markets for Drying Oils

EIGHTY-NINE papers, the largest number in the history of the Society, were presented at the 28th annual fall meeting of the American Oil Chemists' Society, October 11-13, 1954, at the Radisson hotel, Minneapolis, Minn. Twenty-nine papers were divided among four symposia, the remaining 60 papers were presented at six technical sessions. Of the 29 papers presented at the four symposia, 14 papers were presented at the drying oils, seven at the utilization, and four each at the waste disposal and new analytical methods symposia.

Promotion of Drying Oil Research

H. W. Barr of Battelle Memorial reported that he has recently completed a survey on the market potential for fats and oils in drying-oil uses. The primary objectives of this study were a) to determine the factors that have caused drying oils to lose ground in competition with other raw materials, and b) to ascertain the conditions under which drying oils might hope to maintain or improve their competitive position in future years. To accomplish these objectives, personal interviews were conducted with numerous producers and consumers of drying oils and manufacturers of competing synthetic materials.

It is evident from the information gathered that significant shifts in formulation practice have occurred in the drying-oil consuming industries, leading to a marked increase in consumption of synthetic raw materials in lieu of drying oils. This increasing use of synthetic materials stems not only from the superior properties that they impart to some end-products but also from the relatively greater research effort that has gone into their development and application. Dr. Barr stated that it is equally apparent that these past trends will continue in the future unless a major research effort is applied to the drying oils.

As a prerequisite to that research effort there should be an increased recognition of the potential value of drying oils as basic chemical raw materials and a thorough review, evaluation, and dissemination of the results of previous drying-oil research. The research effort itself should be fundamental in character and should include a thorough investigation of a) the basic chemistry of the oils, b) chemical modification of oils, c) formulation of new, more effective products for established or new markets, d) mechanism of film formation, and e) possibilities for developing improved strains of plants from which drying oils are obtained.

S. O. Sorensen also pointed out that edible and industrial applications of fats and oils overlap and are partially dependent upon one another. Factors tending to decrease our edible oil supplies or limiting the availability of soap-making stocks affect the broad picture of drying oil use. This has become increasingly important now that the application of drying oils is no longer essentially the application of linseed oil. Ability to dry well is of secondary importance since present-day chemical modification can convert a semi-drying oil, such as soybean oil, into our second most important drying oil. Consumption figures for oils used in protective coatings in the United States during the past 20 years have doubled. Mr. Sorensen pointed out that we consume per capita each year approximately 43 lbs. of edible fats and use 23 lbs. of inedible fats for paints, soaps, and industrial purposes.

Mechanism of Oxidation

Four papers were presented at the symposium on drying oils on the mechanism involved in autoxidation and polymer formation. L. A. Witting in a paper on the isolation and characterization of the polymers formed during the autoxidation of ethyl linolenate found that the isolated dimer contained 2.4 atoms of oxygen as peroxide, 1.4 as hydroxyl, 3.1 as carbonyl, 4.0 as ester, and none as epoxy group. The trimer contained 3.2 as peroxide, 3.4 as hydroxyl, 4.0 as carbonyl, 6.0 as ester, and none as epoxy group. A portion of the oxygen content of the polymers was not accounted for in this characterization. Since the polymer linkage was broken by ethanolic HCl, it was concluded that the residual oxygen was present in a carbon to oxygen bond linkage which joined monomeric units.

The autoxidation of fats at 60°C. was studied by S. S. Kalbag with a polarograph as a means of distinguishing between different kinds of peroxides. The peroxides formed in methyl esters, and triglycerides of similar composition were compared. Formation of peroxides other than hydroperoxides was observed in greater proportions in fats than in methyl esters. Fractionation using mixtures of acetone and pentane-hexane in different proportions led to the concentration of the non-hydroperoxido peroxide in the acetone soluble fraction. This peroxide is reduced at the dropping mercury electrode at potentials more positive than that for hydroperoxide. Fat oxidized in the presence of 0.1% cobalt drier showed only traces of peroxide reducible in the polarographic cell under the conditions studied. W. O. Lundberg in a panel discussion on autoxidation and oxidative polymerization pointed out that only one free radical was needed to start the oxidation of methyl oleate. E. B. Fitzgerald, another panel member, stated four unsolved problems existed in the utilization of drying oils in protective coatings, namely, better control of wrinkling, yellowing, durability, and drying time.

Modification of Drying Oils

Eight papers in the drying oil symposium involved segregation or modification of drying oils. An automatic 200-tube

SURFACTANTS—Participants in the symposium on the utilization of surfactants are shown above, save for M. Morton of the University of Akron: *(seated)* John Ross, Colgate-Palmolive Company, Jersey City, N. J.; A. M. Schwartz, chairman, Harris Research Laboratories, Washington, D. C.; and C. R. Singleterry, Naval Research Laboratory, Washington, D. C.; *(standing)* Carl Pacifico, American Alcolac Corporation, Baltimore, Md.; V. Dvorkovitz, Diversey Corporation, Chicago; G. L. Brown, Rohm and Haas Company, Baltimore, Md.; and E. I. Valko, Onyx Oil and Chemical Company, Jersey City, N. J.

countercurrent distribution apparatus was used by H. J. Dutton and J. A. Cannon to fractionate linseed oil with pentane-hexane and furfural as solvents. After the application of 800 transfers the weight curve contained four major peaks and consisted of two normal distribution curves, a third partially resolved curve, and a blend of several unresolved curves. The most furfural-soluble glyceride comprises 18% of the total glycerides and, as determined by iodine value and spectrophotometric analysis, is trilinolenin; the next glyceride comprises 12% and is linoleo-dilinolenin; the third partially separated curve comprises 25% and is composed of 2 glycerides with 7 double bonds: oleo-dilinolenin, 20.7%, and dilinoleo-linolenin, 4.3%. Under the random pattern of distribution for fat acids 12.2% linoleo-dilinolenin, 18.2% oleo-dilinolenin, 14.3% trilinolenin, and 3.5% dilinoleo-linolenin are calculated. Since the latter two of these glycerides are not permitted under the strict, even patterns, it was concluded that linseed oil is more accurately described by the random pattern.

R. L. Terrill, one of the panel members, pointed out that drying oils could be modified by physical means, such as thermal polymerization, or by adding something such as styrene. In the latter category E. W. Eckey stated that polyvinyl esters of the higher saturated fatty acids can be made by polymerization of the monomeric vinyl esters, by esterification of polyvinyl alcohol with fatty acid in the presence of a mutual solvent, and by ester interchange between polyvinyl acetate and fats or other esters of the higher fatty acids. The first method is not applicable when drying products comprising unsaturated fatty acid radicals are to be made. The ester interchange method provides a more direct route than the esterification method but requires special conditions for successful operation.

Under suitable conditions polyvinyl acetate reacts with selected esters of higher fatty acids to produce mixed esters in which any desired proportion of the acetate can be replaced by the higher fatty acid radicals. Preferred conditions include the use of a mutual solvent at the beginning of the reaction, a temperature in the range between 50 and 100°C., with an alkali metal alkoxide or an organo alkali compound as catalyst. The reaction may be carried out with or without simultaneous removal of by-product esters by distillation.

The products are viscous oils, soluble in mineral spirits and in other fat solvents. Compared with triglycerides of the same mixed fatty acids, the polyvinyl esters dry more rapidly and form tougher, more scuff-resistant, and more durable films. The polyvinyl esters of mixed higher fatty acids may contain a substantial proportion of saturated fatty acid radicals without graining or clouding. The properties of these esters suggest that they may extend the range of fatty materials useful in the drying oil industries and find use in the formation of products of improved quality.

Other means of modifying drying oils were described by Lewis and by Tess. A. J. Lewis prepared a synthetic "Hysoy" drying oil by the dechlorination of chlorinated soybean oil. Six exterior white paints were prepared having the same pigmentation but differing in vehicle. Vehicles were linseed oil, soybean oil, Hysoy, and blends of Hysoy and soybean oil. Red cedar siding panels were given three coats of each paint and exposed for four years at a 90° angle, facing south, at Peoria, Ill. Paints containing Hysoy compared favorably in durability with those containing linseed and soybean oils.

ANALYTICAL METHODS—Above are the speakers in this symposium: *(seated)* D. H. Wheeler, chairman, General Mills Inc., Minneapolis; R. T. O'Connor, Southern Regional Research Laboratory, New Orleans; and D. S. Bolley, Baker Castor Oil Company, Bayonne, N. J.; *(second row)* R. T. Holman, Hormel Institute, Austin, Minn.; and S. F. Herb, Eastern Regional Research Laboratory, Philadelphia.

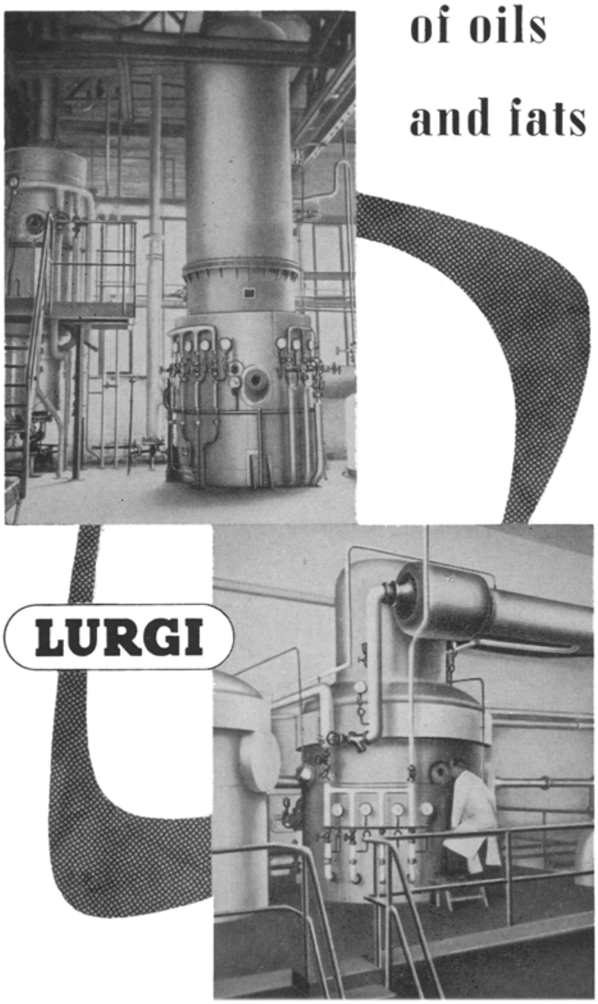
GENERAL SESSION—In this group are *(seated)* L. K. Arnold, Iowa Engineering Experiment Station, Ames; J. H. Gass, Canada Linseed Oil Mills, Montreal; Max Kantor, chairman, Cargill Inc., Minneapolis; and H. M. Teeter, Northern Regional Research Laboratory, Peoria, Ill.; *(standing)* C. T. Smith, Wurster and Sanger, Chicago; R. K. Rao, Iowa Engineering Experiment Station, Ames; F. H. Smith, Sharples Corporation, Philadelphia; S. S. Chang, University of Illinois; and R. O. Feuge, Southern Regional Research Laboratory, New Orleans.

Commercially available epoxy resins derived from epichlorohydrin and bis phenol have noteworthy properties, according to R. W. Tess. In air-drying systems the epoxy resins ordinarily are esterified with unsaturated fatty acids derived from drying oils. These epoxy resins have now been investigated for use as varnish resins for combination with glyceride oils themselves. When cooked with linseed oil, the epoxy resins are very reactive and produce varnishes of high viscosity in approximately half the time usually required for preparation of oleoresinous varnishes. Even straight soy oil can be quickly converted to varnishes of high viscosity when cooked with the epoxy resins. Acidity of the varnishes is very low as indicated by an acid number of two or less.

The epoxy resin-oil varnishes differ in several respects from conventional epoxy esters: they usually contain less epoxy resin; they dry more slowly; they yield softer films; and they have better chalk-resistance in pigmented coatings. The epoxy resin varnishes have unusually good gloss retention and durability when exposed outdoors in clear coatings upon wood. They are superior to ordinary oleoresinous varnishes and oil-modified alkyds in this respect. Small amounts (5%) of epoxy resin also have been found to accelerate greatly the bodying of soy oil. In cooking the varnishes at the high temperatures (580°F.) employed, epoxy groups are destroyed and the total hydroxyl content remains essentially unchanged. At lower temperatures (480°) the alcoholysis of oils by the hydroxyl groups in the epoxy resin proceeds readily while the epoxy groups remain essentially intact.

Twenty more papers involving various phases of autoxidation and modification of drying oils were presented at the technical sessions. Eight of these papers were concerned with model systems of methyl oleate or linoleate. O. S. Privett reported that, in the decomposition of peroxides from linoleate, appreciable proportions of polymeric products were formed whereas, in the decomposition of peroxides from oleate, most of the products were monomeric. Privett also found that the lipoxidase-catalyzed oxidation of sodium linoleate is typically enzymatic and that no chain mechanism similar to that functioning in the autoxidation of methyl linoleate is involved. Methyl oleate autoxidized for short and long periods of time were fractionated with urea by Coleman, Knight, and Swern. Up to a peroxide content of about 15% the autoxidation mixture could be cleanly separated into a peroxide concentrate containing 90% peroxide and unoxidized methyl oleate. From about 15% peroxide to the maximum peroxide content (35-40%) concentration to only about 70% peroxide could be obtained. The remaining material largely was a mixture of oxygenated compounds and residual methyl oleate. If the autoxidation is conducted beyond the peak value in peroxide content, little, if any, concentration of peroxide could be obtained. Also, beyond the peak in peroxide value and in the range of 30-20% peroxide, methyl oleate is substantially absent, and the autoxidation mixture consists almost entirely of oxygenated compounds containing only one functional group in

Extraction and processing of oils and fats



We supply plants and processes for the

- Extraction of oils from oilseeds (LURGI extraction process)
- Recovery and refining of lecithin
- Refining of edible oils
- Hydrogenation of vegetable and animal oils and fats, also of fatty acids
- Distillation and fractionation of fatty acids under high vacuum
- Hydrolyzation of oils and fats under high vacuum without promoter
- Evaporation of soap lye glycerine and saponification glycerine
- Distillation of raw glycerine
- Manufacture of synthetic fatty acids by the oxydation of paraffins
- Manufacture of detergents, sulphonates and cleansers in spray dryers with either atomizers discs (Krause process) or spray nozzles
- High temperatur heating of chemical processing equipment

LURGI GESELLSCHAFT FÜR WÄRMETECHNIK M.B.H.
LURGIHAUS · FRANKFURT AM MAIN · GERMANY

the chain. Evidence was presented which showed that in the autoxidation of methyl oleate substantially all of it undergoes single attack by oxygen (or peroxides) before any significant quantity of multiple attack occurs. α,β-Unsaturated carbonyl compounds are among the important secondary products of autoxidation. Harrison and Wheeler found that methyl stearate with di-t-butyl peroxide gave considerable amounts of higher polymers along with the dehydro dimer. The two chains in the dimer apparently were linked through carbon atoms alpha to the carbomethoxyl group.

Three papers presented at the technical session involved modification of drying oils. D. Aelony found that the phenolic and secondary hydroxyl groups in various phenols could be esterified with fatty acids. The rate esterification was accelerated by catalysts, such as sulfuric acid, phosphoric acid, zinc stearate, lead stearate, and triphenyl phosphite. Reaction time varied from 6 to 168 hours whereas the temperatures ranged from 115° to 250°C. Sulfuric acid was found to be the most effective catalyst, but its use is limited to distillable products because it engenders considerable color.

Paschke and Wheeler found a cyclohexene structure in a monomeric fraction from thermal polymerized eleostearate. They prepared a 50% yield of cyclic isomers of methyl eleostearate by heating the ester in an evacuated ampule as a 10% solution in methyl laurate at 250°C. for 48 hours. The cyclic material was concentrated by distillation and urea treatment. The cyclic concentrate was brominated with one mole of N-bromosuccinimide (NBS) and dehydrobrominated with collidine to aromatize the six-membered ring. The distilled ester was treated with 2 moles of NBS to brominate the chains on the carbons alpha to the ring. The dibromide was hydrolyzed with dilute Na_2CO_3 to the dihydroxy compound, which was oxidized with $KMnO_4$ to phthalic acid. The acid was sublimed as the anhydride, which was characterized by mixed melting points with pure anhydride from another source. The imide was also prepared and checked by mixed melting points.

Surfactants

M. Morton pointed out in the symposium on surfactants that studies of the mechanism of emulsion polymerization have shown conclusively that the surfactant present plays a two-fold role. It not only acts as a stabilizer for the polymer particles which are formed from the monomer, but it also solubilizes some of the monomer within the aqueous phase. The latter phenomenon is of critical importance in the case of water-insoluble monomers since it greatly accelerates the initiation of the polymerization reaction by the water-soluble catalyst present. According to C. R. Singleterry, association colloids of the type designated as micelles are formed in non-polar solvents by the alkali metal, alkaline earth, and certain heavy metal salts of suitable carboxylic, sulfonic, and phosphorus acids as well as of some phenolic compounds. The existence and the physical characteristics of micelles in non-aqueous systems may be investigated by observations of their osmotic properties, viscometric behavior, streaming birefringence, light scattering, or fluorescence depolarization. The structure of such micelles ranges from that of extensive linear polymer-like aggregates to that of small approximately isodimensional units.

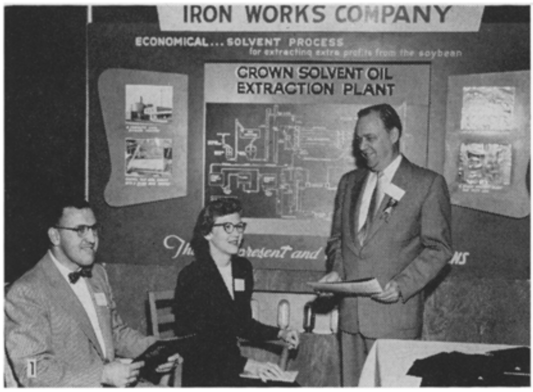
E. I. Valko stated that the most important non-detergent medical use of surfactants is in the control of growth of microorganisms. Cationic, anionic, and nonionic surfactants show various degrees of antibacterial activity. The biological action of surfactants, especially on proteins and blood cells, has been the subject of numerous investigations.

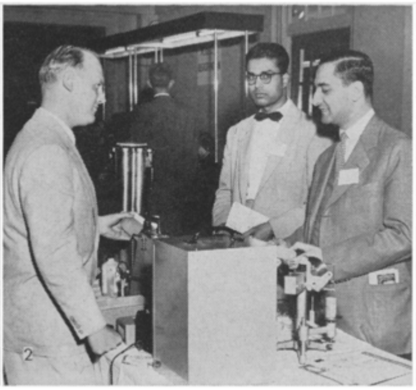
An attempt is made to correlate the biological action and medical use of surfactants with their functional properties when in solution, *i.e.*, their reduction of interfacial tension, absorbability, particularly by an ion-exchange mechanism.

Stability of Edible Fats

Twelve papers involved various phases of fat stability. S. S. Chang found that the characteristic odor of oleo oil and the unpleasant odor of edible tallow could be removed by slight hydrogenation of high selectivity under atmospheric pressure. This hydrogenation process substantially decreased the arachidonic and linolenic acid content of oleo oil and beef tallow by raising their melting points by less tran 2°C.

Three papers were concerned with the use of antioxidants in foods. W. M. Gearhart found that combinations of butylated hydroxy anisole (BHA) and propyl gallate produce the best all-around stability in lard if used at limits authorized by the Meat Inspection Bureau. If only AOM stability is considered,





1. **GIRL CHEMIST—Proving that there is such a thing, Mrs. Barbara Polister of General Mills, Minneapolis, visits with B. W. Nippold, Minnesota Mining and Manufacturing Company, Minneapolis, and A. J. Kaiser, Crown Iron Works.**
2. **CENTRAL SCIENTIFIC COMPANY—C. L. Scripps *(left)* is demonstrating equipment for two visitors: R. K. Rao, Iowa Engineering Experiment Station (and Central Laboratories, Hyderabad, India), and Meny Bergel, University of Rochester (and Rosario, Argentina).**
3. **ATLAS POWDER COMPANY—This concentrating trio is A. L. Sawyer *(left)*, U. S. Department of Navy, Arlington, Va.; T. M. Rinehart, Darco Corporation, New York; and E. M. James, consultant, Swarthmore, Pa. (formerly with Lever Brothers Company, New York).**

propyl gallate alone is the best antioxidant. If carry-through stability, especially at higher temperatures, is the chief qualification, then the best antioxidant is a combination of BHA plus BHT (butylated hydroxy toluene). J. P. West obtained similar results.

Two papers involved a method for the chemical estimation of rancidity and the degree of reversion of an edible oil. S. S. Chang found that the amount of carbonyl compounds diffused from 100 g. of an oil into a stream of nitrogen bubbled through the oil at a rate of 83 cm^3/min. under exactly specified conditions was determined by converting the carbonyl compounds into their 2,4-dinitrophenylhydrazones and then measuring the absorption of the wine-red color of the quinoidal ions at 480 $m\mu$. From the optical density thus obtained, a carbonyl index was calculated and assigned to the oil.

The carbonyl indices of a number of edible oils, such as soybean oil, cottonseed oil, and hydrogenated vegetable oils were found to correlate with the degree of reversion and rancidity of the oils as determined by organoleptic evaluations. The reproducibility of the carbonyl index was good, and its accuracy corresponded to approximately 0.1 point on an arbitrary scale of 1-10 on an organoleptic evaluation system. This method could be used as a means of evaluating the flavor stability of edible oils. The carbonyl index of an oil after aging, at 60°C. for less stable oils and at 100°C. for more stable shortenings, gave a good indication of the flavor stability of the oil.

Refining and Hydrogenation

Nine papers involved various phases of refining and hydrogenation. J. H. Gass described plant trials in which high frequency cavitation in the processing of vegetable oils was used to promote the neutralization of vegetable oils during continuous alkali-refining. Continuous purification and acidulation of vegetable oil soapstock, solvent-extraction, and solvent-holdup as factors in extraction design were also discussed.

R. R. Allen, from a study on the hydrogenation of oleic acid, found that positional and geometrical isomers are formed by a half-hydrogenation, followed by dehydrogenation to form positional isomers that have both geometric configurations. This work has been extended to linoleic acid to determine if the same mechanism applies to an acid with two double bonds. Disruptive oxidation of partially hydrogenated linoleic acid followed by analytical separations of the dibasic acids was used to determine amounts of positional isomers formed during the hydrogenation. The data indicate that the 12-double bond is hydrogenated slightly faster than the 9. Also the double bond in either position migrates equally in either direction to form both positional and geometrical isomers. This suggests that the half-hydrogenation-dehydrogenation mechanism applies to linoleic acid.

New Analytical Methods for Fats and Oils

Six papers on analytical methods in addition to those given in the symposium on new methods were presented at the various technical sessions. Two of them involved the application of chromatography to the separation of the fatty acids of butter fat. Holman separated the fatty acids of butterfat by a proper choice of solvents and concentration of displacer solution. The absorbent used in the experiments consisted of one part Darco G-60 charcoal and two parts Hyflo Supercell. Lauric, myristic, palmitic, and stearic acids were separated in 95% ethanol, using methyl stearate as the displacer. Caprylic and capric acids were separated in 60% ethanol, methyl caprate being the displacer. Single displacement with the corresponding methyl esters of butyric and caproic acid were performed with water and 40% ethanol, respectively.

The application of chromatography and of ultra-violet and infrared spectroscopy were discussed at the methods symposium.

F. A. KUMMEROW

◆

Wish to Interest Students in Chemistry

A recent survey by the Manufacturing Chemists' Association shows that both large and small companies in the industry are attempting to overcome a shortage of scientific personnel by promoting the training of their young men and women, according to Fred J. Emmerich, chairman of the association board and president of Allied Chemical and Dye Corporation. Companies in the chemical industry are awarding about 800 scholarships and fellowships having an annual value in excess of $1,500,000.

They are providing several million dollars annually in prizes to high school students and, in addition, grants-in-aid not specifically tied to scholarship awards and grants to educational institutes in support of research.

Irving Langmuir, Nobel prize winner for achievement in chemistry, has pointed out that young men and women of many different talents and dispositions can find a suitable place in chemistry if they are endowed with curiosity and enthusiasm. Many young chemists find themselves far removed from their original studies, acting as executives in key office positions, market research, purchasing departments, and publications.

An article by Dr. Langmuir entitled "Should Your Child Be a Chemist?" was first published in a series of career advertisements sponsored by a life insurance company. Receiving over two million requests for reprints, the insurance company made the career series available in booklet form.

◆

Fatty Acids Rise

PRODUCTION of fatty acids in August, 1954, totalled 31.6 million lbs., 51.9% above that of the July level, according to the Association of American Soap and Glycerine Producers Inc. Production was 7.3% below that of August, 1953. Total disposition was 30.5 million lbs,. some five million lbs. above the July figures, but approximately two million below the August, 1953 level. Stocks, including work in process, increased to a level of 51.8 million lbs.