ated under automatic constant-composition control in a completely air-free hermetic condition. This is accomplished by utilizing Hermetic pressure centrifuges for all separation in the various stages. The centrifuge used is of the type shown in Figure 7 (6). The material to be separated enters the bowl through the hollow spindle. At the inlet to this hollow spindle is a special feed pump mounted directly on the spindle. By means of this built-in pump the material is forced to the separating zone of the centrifuge bowl. Here separation of the light component (soap) from the heavy component (spent lye or nigre, depending on the stage) occurs. These components then flow respectively to the next processing stage without the need of intermediate booster pumps.

Summary

A new continuous process for the manufacture of soap is described, detailing the three main operations in soapmaking, that is, saponification, washing, and fitting.

In the new process all operations involved in the production of soap are carried out in a hermetically closed system. The amounts of lye necessary for the saponification as well as of brine for the washing and fitting operations are regulated by the automatic constant-composition control system, which eliminates the older method of control of the soapmaking process by cumbersome chemical analyses.

The process is based on the use of the Hermetic separator, a centrifuge of special design which allows the regulation of the separation efficiency during operation and which prevents any admixture or contact of the soap with air and consequently any oxidation of the product during processing.

All types of soap, high grade toilet soap as well as laundry soap and industrial soaps, can be produced by this process, which is characterized by high flexibility, low operation-costs, and a high quality of the finished product.

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X-Ray Diffraction Study of Some Normal Alkyl Thiolesters of Long Chain Acids

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RECENT PUBLICATIONS (2, 3) described the preparation of some normal alkyl thiolesters of long-chain acids. Many of the thiolesters of long-chain fatty acids are solid crystalline materials at ordinary temperatures, suitable for characterization by X-ray diffraction. In this paper long spacings taken from X-ray diffraction powder data are reported for 39 *n*-alkyl thiolesters of normal long-chain aliphatic acids containing an even number of carbon atoms, namely, lauric, myristic, palmitic, and stearic acids. The length of the *n*-alkyl groups attached to sulfur varied from 7 to 18 carbon atoms, with individual groups containing even or odd numbers of carbon atoms.

Experimental

The thiolesters used were those prepared recently by Sasin and Sasin *et al.* (2, 3). The compounds used were crystallized from acetone at room temperature. X-ray diffraction measurements were made with a General Electric XRD-3 direct recording unit, using nickel-filtered CuKα radiation ($\lambda = 1.5405$ A), 1° beam slit, 0.1° detector slit, medium resolution Soller slit, scanning speed 2° per minute, chart speed 60 in. per hour, linear scale, 2-second time-constant. The long-spacing values given in Table I were obtained from oriented unground samples. The unground samples were placed in a thin layer on a glass slide and firmly pressed to insure adherence. The exposed surface of the specimen on the glass slide was approximately 0.5 in. wide by 1.0 in. long. These long-spacing values are the average of at least seven orders taken from the oriented samples. The first and often the second and third orders were not included in the average because of the limited accuracy with which they could be measured. In general, the values given in Table I are precise at least to ±0.05 Å.

Also included in Table I are the relative intensities of the first five orders of long spacing. The relative intensities were obtained as follows. All samples were carefully ground in an agate mortar to minimize orientation. The ground samples were placed in the recess of a plastic holder 1.0 in. long, 0.5 in. wide and 0.015 in. deep and were gently packed to insure adherence. The intensities of the diffraction lines were measured as counts per second at the maximum height minus counts per second of the background, then expressed on a relative scale (I_{Rel}) with the strongest line arbitrarily given a value of 1,000.

The complete X-ray powder-diffraction data for these compounds are not included herein because of the relatively large amount of space that this would require. However the data were sent to the Joint Committee on Chemical Analysis by Powder-Diffrac-

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TABLE I

Long Spacings of Thiolesters of Long-Chain Acids

Compound	Long spacing, Å	Relative intensities of orders of long spacing				
		1	2	3	4	5
n-Heptyl thiolmyristate	25.97	1000	240	23	100	10
n-Decyl thiolaurate	28.00	1000	12	190	1.0	15
n-Octyl thiolmyristate	27.90	1000	190	56	80	3.2
n-Nonyl thiolmyristate	28.92	1000	63	91	76	7.4
n-Heptyl thiolpalmitate	28.85	1000[a]	420[a]	17[a]	86	29
	26.16	1000[a]	420[a]	17[a]	100	51
n-Decyl thiolmyristate	30.30	1000	47	170	42	11
n-Octyl thiolpalmitate	30.25	1000	320	17	170	20
n-Tridecyl thiolaurate	31.15	1000	18	350	12	63
n-Undecyl thiolmyristate	31.17	1000	38	290	32	46
n-Nonyl thiolpalmitate	31.19	1000	210	53	220	6.8
n-Heptyl thiolstearate	31.10	1000[a]	570[a]	18[a]	57	53
	30.40	1000[a]	570[a]	18[a]	60	62
n-Tetradecyl thiolaurate	32.56	1000	8.2	150	26	16
n-Decyl thiolpalmitate	32.53	1000	100	110	150	5.6
n-Octyl thiolstearate	32.51	1000	600	<1	190	80
n-Pentadecyl thiolaurate	33.46	1000	5.2	140	47	15
n-Tridecyl thiolmyristate	33.40	1000	16	290	<1	73
n-Undecyl thiolpalmitate	33.45	1000	17	130	64	5.7
n-Nonyl thiolstearate	33.43	1000	340	14	220	30
n-Hexadecyl thiolaurate	34.83	1000	35	120	95	5.5
n-Tetradecyl thiolmyristate	34.75	1000	<1	190	<1	41
n-Decyl thiolstearate	34.80	1000	170	24	170	6.0
n-Heptadecyl thiolaurate	35.68	1000	38	100	240	1
n-Pentadecyl thiolmyristate	35.70	1000	8.2	240	4.7	52
n-Tridecyl thiolpalmitate	35.66	1000	19	250	15	55
n-Undecyl thiolstearate	35.68	1000	87	52	190	<1
n-Octadecyl thiolaurate	37.10	1000	110	52	160	<1
n-Hexadecyl thiolmyristate	37.13	1000	6.3	190	22	26
n-Tetradecyl thiolpalmitate	37.14	1000	4.3	350	3.6	95
n-Dodecyl thiolstearate	37.10	1000	50	140	110	6.5
n-Heptadecyl thiolmyristate	37.95	1000	5.8	180	38	23
n-Pentadecyl thiolpalmitate	37.92	1000	13	330	<1	120
n-Tridecyl thiolstearate	37.95	1000	11	160	44	13
n-Octadecyl thiolmyristate	39.32	1000	15	100	63	4.6
n-Tetradecyl thiolstearate	39.30	1000	24	240	44	48
n-Heptadecyl thiolpalmitate	40.20	1000	18	310	7.0	92
n-Pentadecyl thiolstearate	40.22	1000	7.1	260	7.8	63
n-Octadecyl thiolpalmitate	41.68	1000	3.1	310	19	56
n-Hexadecyl thiolstearate	41.68	1000	2.8	400	<1	110
n-Heptadecyl thiolstearate	42.45	1000	19	360	4.6	130

[a] Intensity of an unresolved doublet.

tion Methods for inclusion in the X-ray Powder Data File of the American Society for Testing Materials.

Results and Discussion

All the compounds investigated gave X-ray diffraction-powder patterns which contained a large number of sharp and relatively strong diffraction peaks. The thiolesters that contain a different total number of carbon atoms in the molecule are readily distinguished by their long spacings (Table I). However esters that contain the same total number of carbon atoms in the molecule have essentially the same long spacings, in fact, the same interplanar spacings. In these cases it is necessary to rely on the relative intensities of the interplanar spacing, in particular the relative intensities of the long spacings (Table I).

For example, four compounds, namely, *n*-undecyl thiolstearate, *n*-tridecyl thiolpalmitate, *n*-pentadecyl thiolmyristate, and *n*-heptadecyl thiolaurate which contain 29 carbon atoms in the molecule have similar long spacings and side spacings. Apparently the structures of these compounds are isomorphous. Comparison of the relative intensities of the long spacings of *n*-undecyl thiolstearate and *n*-heptadecyl thiolaurate showed that the relative intensities of the 2nd and 3rd orders of the undecyl ester were the reverse of those observed for the heptadecyl ester, permitting the esters to be distinguished. While both compounds have missing 5th orders, the *n*-tridecyl thiolpalmitate and *n*-pentadecyl thiolmyristate have relatively strong 5th orders of comparable intensity, thereby distinguishing themselves from the other two members of the isomorphous series. The variation in relative intensities of the different orders of the latter two compounds is not nearly as pronounced as the first two members; however no difficulty was encountered in identifying an unknown of either structure from a comparison of the relative intensities. The relative similarity in the orders of the long spacings of *n*-tridecyl thiolpalmitate and *n*-pentadecyl thiolmyristate was not unexpected. The heavy scattering group, –COS–, is only displaced slightly from the exact center of the molecule in both cases.

A plot of the long spacings of the thiolesters containing a different number of carbon atoms in the molecule against the total number of carbon atoms in the chains produced two parallel lines. Long spacings for esters that contained an even number of carbon atoms fell on one line while those that contained an odd number fell on the other. The even-membered esters had the slightly greater long spacing. This alternation in long spacing is characteristic of long-chain compounds (1). The average increment in long spacing per carbon atom is about 1.14Å. This is much less than the maximum calculated increment for a carbon atom, 1.306 Å. Therefore the thiolesters crystallize in tilted monomolecular layers. The angle of tilt is about 60°.

In the odd series, compounds containing seven carbon atoms in the S-alkyl chain gave diffraction data that did not conform with the higher members of the series. For example, *n*-heptyl thiolmyristate produced an X-ray diffraction pattern that had a multiplicity of sharp diffraction peaks; its long spacing was not in line with those obtained for the higher members of the series. In addition, *n*-heptyl thiolstearate gave a pattern that indicated the presence of two phases. Twin peaks of comparable intensity were observed, starting with the fourth order. Multiple peaks in the long-spacing region are characteristic of compounds that crystallize in different polymorphic forms. The *n*-heptyl thiolpalmitate also exhibited the presence of two phases in its diffraction pattern. Long spacings calculated for the two phases in each compound have been included in Table I. One long-spacing value of each compound was found to fall in line with those obtained for the higher members of the series. Apparently a portion of these thiolesters had crystallized in the same manner as those of the higher members. The other long-spacing value obtained from the diffraction data of *n*-heptyl thiolpalmitate and thiolstearate was about an angstrom less than that of the expected form of each compound. These values were then compared with the long-spacing value obtained for the single phase of *n*-heptyl thiolmyristate. A plot of these long spacings against the total number of carbon atoms in the molecule yielded a straight line. This indicated that the second phase present in both *n*-heptyl thiolpalmitate and thiolstearate was identical in packing to that of the single phase found for *n*-heptyl thiolmyristate. Apparently thiolesters of long-chain fatty acids containing seven carbon atoms in the S-alkyl chain possess a structure such that each of two modes of packing are equally possible. Thiolesters containing five carbon atoms in the S-alkyl chain (4) did not show any indication of forming more than one crystalline form. This crystalline form corresponded to that found for *n*-heptyl thiolmyristate, which was different from that of the higher members of the series. It appears that a change in packing of the odd esters takes place below a mercaptan chain length of about seven carbon atoms.

The lower members of the even series, namely, *n*-hexyl thiolstearate and thiolpalmitate, yielded a single phase unlike the odd heptyl derivatives previously discussed. The long spacings of the hexyl derivatives were only a few tenths of an angstrom unit less than the values expected by extrapolation of the long spacings of the higher members of the series. This is different from the odd series in which the difference in long spacing because of the change in packing form is relatively large, about an angstrom unit. It should be pointed out that the *n*-hexyl derivatives melt close to room temperature, and special precautions had to be taken in order to obtain their X-ray diffraction pattern, thereby reducing the precision of the determined long-spacing value. Thus it could not be shown with certainty that a change in packing occurred below a mercaptan chain length of eight carbon atoms in the even series.

Summary

X-ray diffraction-powder data are reported for 39 *n*-alkyl thiolesters comprising four different series, namely, lauric, myristic, palmitic, and stearic acids. All individual compounds can be identified and distinguished by the X-ray diffraction data. Compounds containing the same total number of carbon atoms in the molecule have the same long and side spacings but differ in the relative intensities of the various orders of the long spacings. The esters crystallize in tilted monomolecular layers. The long spacing is a function of the total carbon content of the molecule and forms two series, one for the odd members and one for the even members. A change in the structure-type definitely occurs in the odd series on decreasing alkyl chain-length below 9 carbons.

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Report of the Cellulose Yield Committee, 1958-59

THREE SETS OF SAMPLES were sent out during the year 1958–59 to nine different laboratories. The following table gives the average results for the three tests.

The checks between the laboratories during the past year were excellent. Checking out of the samples however should be continued as occasionally some laboratory sends in a bad analysis, which is immediately picked up by running these checks.

Lab. No.	No. of tests	A Linter	B Linter	C Litner	Over-all average for the year
1	3	78.7	75.0	70.2	74.6
2	3	78.6	74.6	69.3	74.1
3	3	78.2	74.2	69.6	74.0
4	3	78.5	74.8	70.1	74.4
5	3	78.5	74.8	70.1	74.4
6	3	78.9	75.1	70.3	74.7
7	3	78.3	74.3	69.5	74.0
9	3	78.2	74.1	68.6	73.6
10	3	78.4	74.6	70.0	74.3
		78.4	74.6	69.7	74.2

It might be interesting to reflect that this committee has been in operation for approximately 22 years without any serious complaint in regard to cellulose yield by customer or seller. This is an excellent record for this method.

No changes are recommended for the method at this time. It is recommended that samples be sent out three times during the next year to check different laboratory equipment.

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