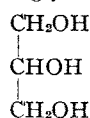


Glycerine Derivatives, Their Properties and Uses¹

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THE ANNUAL glycerine production of the United States is in the neighborhood of one hundred forty million pounds. Of this production a very large percentage is used and consumed unchanged, as the glycerine is employed on the basis of its physical properties as a solvent, plasticizer or hygroscopic agent. The only major outlets for glycerine based on its chemical properties are as nitroglycerine, mono-glycerides and alkyd resins. In view of the fact that these compounds are only three of the large number of glycerine derivatives known it seems desirable to call attention to some of the other derivatives since the possibilities of providing "tailor-made" molecules by modification of the functional groups of the glycerine structure have not been fully appreciated. The three hydroxyl groups of the glycerine molecule are quite

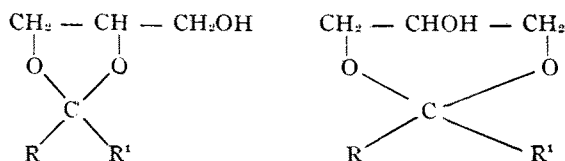


susceptible to a number of chemical alterations. Among these may be cited the formation of ethers, esters, amines, halides and sulfur compounds. By varying the extent, type and combination of the substituents it is possible to produce compounds of widely varying physical and chemical properties. An attempt will be made in this paper to describe the preparation and characteristics of the most common types of glycerine derivatives and to suggest uses and research problems in this field.

ACETALS AND KETALS

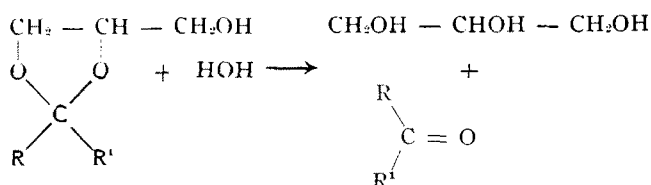
Glycerals and glyceryl ketals are formed by the condensation of glycerine with aldehydes or ketones, by elimination of water. Small amounts of acid catalyze these reactions. The formation of the product quickly and in good yield may be facilitated by continuously removing the water formed as an azeotropic mixture (470).

By proper choice of the aldehyde or ketone it is possible to vary the physical properties of the product from a medium-boiling, water-soluble liquid to a high-boiling, water-insoluble liquid. Chemically these products ordinarily consist of mixtures of isomers having 5- and 6-membered rings, viz.:



The isomers are usually difficult to separate. Products of this class are in general capable of functioning as solvents for cellulose esters and in some cases for cellulose ethers. Some are also useful as plasticizers.

These compounds are hydrolyzed slowly by water, and more rapidly by acids, to give glycerine and the aldehyde or ketone:



This may be an advantage in some cases, because it offers a useful method for the slow liberation of aldehydes and ketones. By this means a small continuous concentration of aldehyde can be maintained in a system, for example, as a preservative. Volatilization of the aldehyde is balanced by further hydrolysis.

Table I gives a list of some of the more common glycerals and glyceryl ketals with their densities and boiling points.

TABLE I.

Glycerine-	d.	b. p. (or m. p.) °C.	Reference Notes
acetaldehyde	1.131 ²⁵ ₄	185.7 ⁰⁰	1-5, 17
acetone	1.063 ²⁵ ₄	201.7 ⁰⁰	2-3, 6-12, 23,27
acetophenone	1.2382	142.1 ⁰ 134.5	13-14
benzaldehyde	1.190 ²⁵ ₄	145-52 ³	2-4, 6, 15-6
n-butaldehyde	1.054 ²⁰	84.7 ³ 214.7 ⁰⁰	3, 470
cinnamaldehyde		m.p. 110-2	18-9
chloral	1.5500 ¹⁷	142-4 ¹¹	10, 20-2
cyclohexanone		145-50 ¹³	23
formal	1.2198 ²⁵ ₂₅	195.7 ⁰⁰	2-3, 18, 24-5
furfural	1.277 ²⁶	267-8.7 ⁰⁰ 154-6.1 ⁴	3, 470
methyl ethyl ketone.....		113.5	26
di-propyl ketone		160	26

General References: 28-9

HALOGEN COMPOUNDS

Except for special uses, the only commercially important halogen derivatives are the chlorohydrins. Of these, the 1- and 1, 3-derivatives are the easiest to prepare and have therefore been given more attention than the 2- or β-substituted compounds. The 1- and 1, 3-derivatives are made from hydrogen chloride and glycerine in the presence of a small amount of catalyst such as glacial acetic acid. The extent of the reaction is controlled easily by proper regulation of temperature and extent of absorption of hydrogen chloride. The products usually contain small amounts of β-substituted compounds and large proportions of normal 1- or 1, 3-substituted derivatives.

The mono-halohydrins are soluble in water in all proportions, the di-halohydrins are only slightly soluble, and the tri-halo compounds are insoluble in water. The more highly substituted derivatives have found use as solvents for natural and synthetic resins.

The halohydrins are important as intermediates in the synthesis of other glycerine derivatives such as ethers,

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thiocyanates and certain mixed derivatives containing different functional groups.

The more important halohydrins are listed in TABLE II.

TABLE II.

Compound	d.	b. p. °C.	Reference Notes
α -Chlorohydrin	1.318 ²⁵ ₂₅	136-42 ⁴⁰	29-54, 71
α, γ -Dichlorohydrin ..	1.3591 ²⁵ ₂₀	172-87 ³⁶	29-54, 71
β -Chlorohydrin	1.328 ₀	146 ₁₈	44, 51, 55-8, 71, 469
α, β -Dichlorohydrin ..	1.3551 ⁷ ₃	182	44, 51, 55-8, 71, 469
α -Bromohydrin	?	?	59-60, 469
α, γ -Dibromohydrin ..	2.11 ₁₈	219	59-60, 469
β -Bromohydrin	?	?	61-2, 469
γ -Iodohydrin	2.03 ₁₈	63-4, 67, 469
Tribromohydrin	2.436 ²³	220	65-6
Trichlorohydrin	1.417 ₁₅	158	54, 68-70

ESTERS

The esters of glycerine comprise a large and important group of derivatives. Perhaps the best-known examples of this group, other than the fatty glycerides, are nitro-glycerine, triacetin, ester gum and the alkyd resins. These last two compounds are of especial importance in the protective coating field. Ester gum, which is the glycerine ester of abietic and other acids occurring in rosin, is of primary importance in varnish and lacquer formulation. It is prepared simply by heating rosin and glycerine until the reaction is practically complete. The alkyd resins, which are basically polymerized glycerine phthalate in combination with various modifying agents, are widely used in enamels, lacquers and varnishes.

While the alkyd resins represent one of the most important outlets for glycerine, this subject is so highly specialized that it will not be discussed here. It is thoroughly covered by Ellis in his book on Synthetic Resins (471).

Esters of most of the common organic acids have been prepared, but with the exception of triacetin, which is used as a plasticizer, there has apparently been little effort to exploit them commercially. Glycerol monostearate, laurate, oleate, and monoricinoleate are sold principally as emulsifying agents. A modified glyceryl borate is advertised as a lubricant, softener, plasticizer and adhesive.

Glycerophosphoric acid and glycerophosphates have received extensive study and have found use as emulsifying agents, plant and seed stimulants, and in medicine (125-75).

Glycerol partially esterified with long-chain fatty acids gives rise to the so-called "superglycerinated fats," which are useful as emulsifying agents, for example, in such foods as peanut butter and margarine.

Uses for a few of the less common esters are mentioned in the literature. For example, the glycerides of salicylic acid are proposed for treatment of sunburn (179-92); glyceryl monocinnamate is mentioned as a remedy for scabies (110); glyceryl monochloroacetate is described as an insecticide (88-9); glyceryl formate is reported to be used in a dentifrice (112); glyceryl orthosilicate is said to have some use in medicine (91); glyceryl oxalate is reported to be hard and glassy and might therefore be an interesting type of resin (91). Ellis (471) describes a number of additional glycerine esters of various acids which have been suggested from time to time for use in the resin field. With one or two exceptions these have not been commercialized. Accord-

ing to a British patent (106), glycerol carbonates can be prepared by heating glycerol with phosgene in the presence of amines. They are reported to be useful in therapeutics.

The lower alkyl formates are reported to be good insecticides but are inflammable. Some of the glyceryl formates might have the desirable properties of the products reported while being less inflammable.

Table III lists some of the more common glyceryl esters and some of their physical constants.

TABLE III.

Glyceryl—	d.	b. p. (or m. p.) °C.	Reference Notes
monoacetate, α	1.2060 ²⁰ ₄	129-31 ₈ 158 ₁₀₅	7, 47, 72-4, 86
monoacetate, β	1.20	158 ₁₀₅	15
diacetate, $\alpha\gamma$	1.1779 ¹⁵ ₁₅	175-6 ₄₀	74-9, 469
diacetate, $\alpha\beta$	1.1173 ¹⁵ ₄	172-3.5 ₄₀	80
triacetate	1.1606 ¹⁵ ₁₅	258-9 ⁷⁵ ₆	78, 81-5, 87, 469
monochloroacetate	88-9
trichlorotriacetate	89-90
monobenzoate, α	m.p. 36	469
tribenzoate	1.228 ₁₂	m.p. 76-6.5	91-3, 469
borate	Resinous	91, 94-103
mono-n-butyrate, α	1.1344 ²⁰ ₄ 1.088 ₁₇	139-40 ₄	73
mono-iso-butyrate, α	264-6	86, 469
tributyrate	1.0350 ₂₀	315	104-5
carbonates	m.p. 148	106-9, 469
monocinnamate	oil	110, 469
citrate	47
monoformate	1.5052 ₀	160-70 ²⁰⁻³⁰ 154-7 ₁₀	81, 86, 111-2, 116-7, 120
diformate	1.3209 ₀ 1.305 ^{18.3} ₀	148-9 ₁₅ 158-60 ₁₈	81, 111, 113, 115-6, 118-20
triformate	1.320 ₁₈	266 ⁷⁰² m.p. 18	81, 114, 116, 120 469
monolactate	sirup	121-3, 469
monolaurate, α	m.p. 59	93, 124, 469
trilaurate	0.8944 ⁶⁰ ₄	m.p. 45-6	93, 124, 469
oxalate	91, 107, 176
monopropionin	1.1537 ²⁰ ₄	132-4 ₈	73, 86
dipropionin	170-3 ₁₀	90, 469
tripropionin	1.100 ²⁰ ₁₈	130-2 ₈	177-8
monosalicylate, α	m.p. 76	469
trisalicylate	m.p. 79	179-92, 469
orthosilicate	amorphous powder	91, 193-4, 469
monostearate	m.p. 78	93, 124, 469
monosulfate, α	unstable	91, 195, 469
tannate	196

General references: 15, 197-204

ETHERS

The glyceryl ethers have widely varying properties depending on the type and number of ether radicals in the molecule. They range from low-boiling liquids to high-boiling solids, materials of complete water solubility to others of total insolubility. Many of the common ethers have been prepared, and some have been studied for commercial utilization where they have been shown to have value as solvents and as resin intermediates.

There are three general methods of preparation. For the aliphatic ethers the best method seems to consist in

treating the chlorohydrin with a large volume of the alcohol containing sodium or potassium hydroxide. The aromatic ethers are easily prepared by treating the sodium or potassium salt of the phenol with the chlorohydrin. The third method of preparation employs sodium glyceroxide (q.v.) and the alkyl bromide. This method is not satisfactory with simple alkyl chlorides but when other groups such as the phenyl group are attached to the carbon atom carrying the chlorine atom, the latter is then sufficiently labile to react.

The cyclic ethers should also be included in this group. The substance of this type most closely related to glycerol is glycidol, or glycide, which is prepared from monochlorohydrin and alkali. Although these substances are not very common, they are not particularly difficult to prepare, and they offer interesting possibilities as solvents and as intermediates for synthesis, since the oxide ring is quite reactive. An interesting new use for these compounds is as bactericides and fungicides.

The glyceryl monoaryl ethers are reported to be useful as wetting agents and detergents and in resin production. The completely substituted ethers seem to offer possibilities as water substitutes for high temperature-low pressure boilers, especially since the properties can be varied easily by a suitable choice of substituents. Some of the partially substituted ethers have been proposed as hydraulic fluids.

Table IV lists some of the common glyceryl ethers, together with some of their important properties.

TABLE IV.

Glyceryl- Ether	d.	b. p. (or m. p.) °C.	Reference Notes
a-Isoamyl	0.987 ²⁵ ₂₅	137-9 ²⁷ 251-2 ⁷⁵⁸	15, 206
a, γ-di-Isoamyl	0.903 ²⁵ ₂₅	147-53 ¹⁰ 269	206
a-Benzyl	1.196 ¹⁵ ₁₅	124-6 ₂	15, 206-7
a-n-Butyl	0.945 ²⁵ ₂₅	133-7 ₁₈	208
Cresyl			209-12
a-Ethyl	1.063	231-2 ⁷⁶²	15, 206, 208
a, γ-di-Ethyl	0.920 ²¹	190	206, 213-6
tri-Ethyl	0.886 ²⁵ ₄	103-5 ⁶⁰ 181 ⁷⁶⁰	206
Epithylin	0.94 ₁₂	128-9	216-7
Glycidol	1.1143 ²⁸	41 ₁	218-30
a-Methyl	1.1147 ²⁵ ₂₅	110 ₁₈ 221 ⁷⁵⁴	206-7, 231-5
β-Methyl			236
a, γ-di-Methyl	1.003 ²⁵ ₂₅	69.5-70.5 ¹⁵ 164-70 ⁷³⁶	206-7, 214, 216, 237
tri-Methyl	0.937 ²⁵ ₄	148 ⁷⁰⁸	206-7, 237
Epimethylin	1.002 ₆	113-4 ⁷⁷⁰	238
mono-α-Naphthyl		m.p. 91-2	469
mono-β-Naphthyl		m.p. 109-10	210-2, 239, 469
a-Phenyl		185-7 ₁₅ 150-5 ₄ m.p. 53-4	210-1, 215, 217, 239-41
a, γ-di-Phenyl		287-8 m.p. 80-1	85, 119, 212, 215, 217, 241-2
a-o-Cl-Phenyl		m.p. 56	469
a-p-Cl-Phenyl		m.p. 76	243-4, 469
mono-2, 4-di-Nitro-phenyl		m.p. 83	245-7, 469
Epiphenylin	1.08 ²⁵ ₄	115-6 ₈₋₄	216-7
a-Propyl	1.074 ¹⁸ ₄	118-22 ₁₅	208
a, γ-di-Isopropyl	0.917 ₁₅	112-3	469
a, γ-di-n-Propyl		215-7	206, 469
mono-p-Tolyl		m.p. 73-4	206, 242, 469

General References: 206, 215-7, 239, 248-52

METAL GLYCERATES

Many of the common metal salts of glycerine have been prepared. Since glycerine is such a very weak acid, the salts are in general strongly alkaline. Probably the three most common salts are those of sodium, calcium and lead. Sodium glyceroxide, which is prepared by heating glycerine with sodium hydroxide, (205-6, 245, 253) is very hygroscopic. It is used in preparing glyceryl ethers by reaction with organic halides; it has also been proposed as a drying agent, e.g. in the preparation of absolute alcohol. Calcium glyceroxide (232, 254-8) is very hygroscopic, and absorbs carbon dioxide readily. These two properties may indicate its greatest possible usefulness. Lead glyceroxide (259) is a well-known cementing material. It is reported to be a catalyst in the formation of alkyd resins (260). Glycerine forms complex metal compounds with copper, iron and other metal hydroxides in the presence of the alkali metal hydroxides. The reaction with copper hydroxide is used as a basis for one method for the estimation of glycerine.

OXIDATION PRODUCTS

Glycerol can be oxidized to give a number of products. Isolation of these materials in a pure state is in general difficult. According to the literature, the following may be prepared fairly readily: dihydroxyacetone (261-81); glyceraldehyde (91, 261, 263, 268-9, 279, 281-7) and glyceric acid (91, 268-9, 279, 296-301).

There is a reference (288) to the possible role of glyceraldehyde in the prevention of the development of cancer cells. Citric acid (302-3) and pyruvic acid (304) have also been prepared from glycerine. Glyceraldehyde (291) and dihydroxyacetone (289-95) are reported to have the ability to protect the heart against the toxic action of cyanides.

REDUCTION PRODUCTS

The principal reduction product of glycerine is propylene glycol which is easily derived by the catalytic hydrogenation of glycerine. This glycol has properties more nearly resembling ethylene glycol than glycerine. It is being produced in large quantities as a by-product of the petroleum industry.

MISCELLANEOUS GLYCERINE DERIVATIVES

There are many glycerine derivatives of present or potential importance which are not included in the general classes listed above. Some of these will be discussed in this section, and a few new derivatives will be suggested as worthy of study.

An interesting compound which can be prepared by the thermal decomposition of glycerine is acetol, CH₃ — CO — CH₂OH (269, 305). It has been proposed as a solvent, but it should also be of value as an intermediate in chemical synthesis as it is very reactive. It undergoes addition reactions readily, besides having the usual carbonyl and primary alcohol reactions.

Acrolein (283, 306-59) is formed from glycerine by the action of dehydrating agents such as potassium bisulfate. It is a low-boiling, unstable, reactive unsaturated aldehyde, and has found use in resin formation, as an antiseptic, as a warning agent in gas lines, and in tanning. The preparation of thioacrolein has been patented (360).

The preparation of allyl alcohol (111, 118, 120, 312,

361-8) from glycerine is a standard method of making this alcohol.

The amino derivatives of glycerol have not received so much attention as they would seem to deserve. These materials have found some use in therapeutics and in removing carbon dioxide and hydrogen sulfide from gas mixtures. Some of these products should make excellent soaps with the higher fatty acids. Since so little is known (2, 226, 369-405) about these amines, and since they have such interesting properties, it seems that they would be worthy of further study.

The cyclic compounds benzanthrone (406-9), dihydroxybenzanthrone (410-11) and quinoline, (412-3) are prepared from glycerine and, respectively, anthraquinone, alizarin and aniline. These substances find uses in dye-making and in therapeutics.

A cashew nut oil-glycerine product has been suggested as a rubber substitute (414-6). A substantially water-insoluble plastic product suitable for molding has been prepared from glycerine and carbohydrates such as dextrose (417).

The combination of iodine, zinc iodide and glycerine is marketed under the name of Talbot's solution; a similar product containing phenol in addition is called Boulton's solution (418). It is claimed that these preparations are readily adsorbable and non-irritating sources of iodine for medical use.

The polyglycerols (419-36) form an interesting and useful class of compounds. They are prepared by condensing glycerine with itself in the presence of alkalis, iodine, etc., and are polyhydroxy ethers containing 6, 9, 12, etc., carbon atoms. They are high-boiling and viscous and have properties somewhat similar to those of glycerine and give derivatives comparable with those of glycerine.

Certain esters of polyglycerols have found use as plasticizers (437-8).

The depolymerization of starch by heating with glycerine has been described (439-40).

Mixtures of glycerine derivatives containing sulfur have been prepared by treating glycerine and certain glycerine derivatives with sulfur or sulfur compounds. In some cases pure compounds can be isolated, whereas otherwise mixtures result. Certain of the products have found use as emulsion ripeners or rubber substitutes (91, 441-50). Glyceryl xanthates might well be mentioned in connection with other sulfur compounds. They are prepared by treating glycerine or sodium glyceroxide with carbon bisulfide (451). Sodium glyceryl xanthate has been used with some success as an ore flotation agent and as a rubber accelerator. It is possible that modification of the glycerine residue in this molecule in one of the many possible ways would have a definite effect on the properties. Certain of the sulfur-bearing derivatives might be expected to have value as insecticides. Among the most promising of these are the thiocyanates and xanthates. The possibilities are particularly attractive because the properties of the basic compounds can be varied by introduction of other groups, making it possible for example to synthesize a molecule containing two groups known to have insecticidal properties. Since these possibilities have not been investigated very thoroughly, a very promising research field is awaiting development.

Thioglycerol, which can be prepared from monochlorohydrin and potassium acid sulfide has been reported as effective in healing wounds (452-3).

MIXED DERIVATIVES

This heading is intended to cover those derivatives of glycerine which contain more than one functional group. Perhaps the best-known example is epichlorohydrin (48, 50, 52, 63, 371, 454-68). Others are: monoacetin monoethylether, dichlorohydrin propionate, acetone glycerol methyl ether, and the chlorohydrin ethers, which can be prepared from epichlorohydrin and alcohols. Literally hundreds of compounds of this type have been prepared, and the possibilities are unlimited as the properties of such compounds can be modified in any desired direction. Thus it is possible to combine the properties of ethers and esters in the same compound and by the proper choice of substituent groups obtain compounds of properties ranging from those of the simplest aliphatic compounds to those of high molecular weight aromatic compounds. While a large number of glycerine derivatives containing several types of functional groups have been prepared there has been little attempt to commercialize them with the exception of the modified alkyd resins which may be considered as esters of phthalic and fatty acids.

SUMMARY: The subject of glycerine derivatives is reviewed. The compounds are discussed according to types, and properties and uses are listed. An attempt is made to suggest new uses and to indicate possible new compounds of commercial interest.

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Use of Indicators for Showing the End Point of The Swift Fat Stability Test on Lards

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THE Swift Fat Stability Test has been in common use for measuring the keeping quality of lards. (1) The end of the induction period is determined by organoleptic means, and then confirmed by titration of the peroxides formed. The objection to this procedure is that it is difficult to determine the end of the induction period by smelling if the lard is not neutral to begin with. There is the personal factor involved, i.e., no two operators will sense the end of the induction period at exactly the same time. Also, there is a tendency to omit the confirmatory test of titrating the peroxides and to rely solely upon smelling for determining the end of the induction period. The author proposes to replace organoleptic tests and peroxide-titration by causing a color change of suitable indicators at the end of the induction period, similar to the scheme of Stebnitz & Sommer in determining the keeping quality of butter (2).

Theory: This method is based on the production of volatile fatty acids in the lard at the end of the induction period, due to hydrolysis of the peroxides formed during the oxidation of the lard. Powick has shown that the fatty acids formed from the splitting of high molecular weight acids were the lower molecular weight acids and that most of the saturated acids up to C9 have been identified (3). Powick has shown that at the end of the induction period there is a rapid increase of volatile fatty acids distilled over by bubbling air through fat at 100°C. (4). The author has found that the quantity of fatty acids distilled over by bubbling air through 20 gms. of rancid lard overnight is equivalent to 4.0 cc. of 0.1 N NaOH.

Method: Air is allowed to bubble through lard (at 100°C.) and then through 10 cc. of indicator solution, respectively. When the indicator, contained in a test tube, changes color, the end of the induction period has been reached. Stebnitz and Sommer employed methyl red for use with butter (2). The author found methyl red unsatisfactory for use with lard; the color change usually occurred one to two hours after the end of the induction period had been passed. Alizarin red S and Brom Cresol Green gave consistent results which checked with results obtained by the original Swift's Methods. (See Table I.)

Directions for preparing indicators:

1. Brom Cresol Green: Triturate 0.1 gm. of the indicator with 14.3 cc. 0.01 N NaOH, and dilute

to 250 cc. with water. Further dilute 1 cc. to 10 cc. before using.

2. Alizarin Red S. (Alizarin Mono-sodium Sulphonate). Make a 0.1% solution in water.

TABLE I.

Lard Sample	Indicator Used	Peroxide Value When Indicator Changed Color	Stability
A	Alizarin Red S	30 milliequivalent of oxygen	3 hours
B	" " "	26 " " "	14 hours
"	" " "	19 " " "	12 hours
C	" " "	40 " " "	14 hours
"	" " "	46 " " "	13 hours
"	" " "	61 " " "	13 hours
"	" " "	65 " " "	10 hours
D	" " "	40 " " "	10 hours
"	" " "	25 " " "	12 hours
"	" " "	20 " " "	12 hours
E	" " "	52 " " "	13 hours
"	" " "	63 " " "	14 hours
"	" " "	21 " " "	14 hours
"	" " "	30 " " "	14 hours
F	Alizarin Red S	21 " " "	12 hours
"	Brom Cresol Green	21 " " "	12 hours
G	Alizarin Red S	25 " " "	14 hours
"	Brom Cresol Green	27 " " "	15 hours
H	" " "	14 " " "	5 hours
I	" " "	54 " " "	3 hours
J	" " "	46 " " "	3 hours
K	Brom Cresol Green	23 " " "	2 hours
"	" " "	25 " " "	4 hours
"	" " "	40 " " "	3 hours
"	" " "	17 " " "	3 hours
"	" " "	29 " " "	2 hours
"	" " "	23 " " "	2 hours
L	Alizarin Red S	29 " " "	6 hours
"	" " "	20 " " "	5 hours
"	Brom Cresol Green	21 " " "	6 hours
"	" " "	32 " " "	4 hours
M	No indicator	40 " " "	6 hours
"	" " "	29 " " "	6 hours
"	Alizarin Red S	40 " " "	5 hours
"	" " "	36 " " "	6 hours
"	Brom Cresol Green	21 " " "	6 hours
"	" " "	25 " " "	5 hours

Summary: In determining the keeping quality of lards by use of the Swift's Fat Stability Test, pH indicators may be used to replace the organoleptic means and peroxide-titration for ascertaining the end of the induction period. This does away with the personal factor and is more convenient for the operator. Instead of smelling the several tubes and then titrating the peroxides produced in the lards, the operator needs merely to glance at the test tubes containing the pH indicator in order to determine whether or not the end of the induction period has been reached.

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