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Camphor Substitutes in the Manufacture of Celluloid¹

By Albert Parsons Sachs and Oscar Byron

1523 MADISON AVE., NEW YORK, N. Y.

The history of celluloid manufacture is so well known that to recount it here would be superfluous.² Alexander Parkes³ observed that nitrocellulose, camphor, and alcohol are of service in the preparation of horn, rubber, and gutta-percha imitations. A few years later Daniel W. Spill⁴ gave his famous formula for the gelatinization of nitrocellulose by ethyl-alcoholic solution of camphor, followed by kneading of the plastic mass between rolls. The Hyatt brothers⁵ worked out the technical details for the large-scale manufacture, gave the product its name, "celluloid," and made it an article of commerce.

The uses of celluloid are extremely varied, and even a list is too large for the scope of this paper.⁶ Suffice it to note that celluloid has entered as a material into so many fields that it is no longer considered primarily as a substitute for, or imitation of, other materials (horn, ivory, bone, tortoise shell, onyx, agate, etc.), but rather as a basic raw material which resembles these others in appearance or other properties, but is valuable chiefly because of its own properties, *i. e.*, its strength, its chemical resistance, its transparency, its brilliant colors in the opaque form, its latent plasticity, etc. Every valuable primary raw material is sooner or later imitated, and celluloid is no exception to this rule. The attempt has been made and is still being made to find a celluloid substitute. It must cost less than celluloid, retain practically all the valuable properties of celluloid and have other valuable properties of its own, while losing some of the unfavorable properties of celluloid. And let it be said at once that this search has by no means been unsuccessful. New products have been invented, some with particularly valuable properties, but all of them have only limited applications. Bakelite,⁷ for instance, has come prominently into the field of plastic products, bringing with it some extremely valuable properties and making for itself a distinctive place without really competing with celluloid.

Certain disadvantageous properties of celluloid are well known to everybody.

1—It is easily inflammable.

2—It has a marked and none too pleasant odor.

3—The temperature at which celluloid becomes plastic is not far below the temperature at which the first evidence of decomposition appears.

Of course, celluloid possesses certain other properties, which may be improved. For instance, the elasticity may be improved until it approaches that of ivory, in which case celluloid could be used for billiard balls.

¹ Received February 7, 1921.

² *Kunststoffe*, **1914**, 277; *THIS JOURNAL*, **6** (1914), 156, 440.

³ Brit. Patent 1313 (1865).

⁴ Brit. Patent 3102 (Oct. 1869) and U. S. Patent 97,454 (Nov. 30, 1869).

⁵ *THIS JOURNAL*, **6** (1914), 156, 440; U. S. Patent 105,338 (July 1870).

⁶ F. Sproston, *J. Soc. Chem. Ind.*, **39** (1920), 352; J. H. Stevens, "Raw Material," **1**, 227.

⁷ See H. Lebach, *Chem.-Ztg.*, **37**, 733, 750.

CELLULOID SUBSTITUTES

A long series of attempts has been made to obtain a product in place of celluloid without its disadvantages, and having the further advantage over celluloid of a lower price. In carrying out these attempts the lines of development have followed several directions:

1—Products not based on cellulose esters, such as:

(a) Casein derivatives;¹ (b) gelatin derivatives;² (c) phenol-formaldehyde condensation products;³ (d) resin derivatives, etc.⁴

2—Products based on cellulose esters other than cellulose nitrate such as:

(a) Acetate⁵ (especially "cellon"); (b) xanthates;⁶ (c) mixed esters.⁷

3—Products based on cellulose nitrate but with a substance other than camphor ("camphor substitute") as the nonvolatile solvent or gelatinizing agent.

Classes 1 and 2 will be discussed in later papers and the third class only in the present paper.

CELLULOID

It will not be amiss to discuss very briefly the nitrocellulose camphor product known as celluloid.⁸

COMPOSITION—Celluloid (the common name for all pyroxylin plastics) is a solid solution of nitrocellulose and camphor (or camphor substitute) which becomes plastic on being heated. The camphor (or camphor substitute) may be considered as the solvent and the softening and plasticifying agent. The more camphor (or camphor substitute) the celluloid contains the more easily it softens and the lower is the temperature at which it becomes plastic. The higher the proportion of nitrocellulose the more elastic (in the exact, scientific sense of "elastic") is the celluloid, as well as harder and more resistant. Not every nitrocellulose yields a plastic product with camphor; only those are suitable for celluloid manufacture which are completely soluble in a 10 per cent solution of camphor in alcohol. Only a part of the camphor in celluloid can be sublimed out or driven off by heat; 10 to 15 per

¹ "Galalith," for instance, D. R. P. 141,309 and 147,994 (1903).

² For instance, L. Trommer, D. R. P. 278,667 (April 27, 1913).

³ See C. F. Chandler's Perkin Medal Presentation Address, Award to L. H. Baekeland, *THIS JOURNAL*, **8** (1916), 179.

⁴ D. R. P. 49,507 (March 13, 1889), Wallerstein and Knoll, celluloid substitute for picture frames is made by adding a solution of borax or potash and a dye to melted white shellac, then a fibrous binding material like asbestos and a filler of lithopone or zinc white.

⁵ Cellon is manufactured by the Rhein-Westf. Sprengstoff A.-G. at Cologne and consists of cellulose acetate and camphor substitutes. It is practically noninflammable.

⁶ French Patent 188,823 (January 19, 1906), Soc. Française de la Viscose.

⁷ For instance, U. S. Patent 1,354,726 (Carroll) of Oct. 5, 1920, employing cellulose nitrate and cellulose acetate with tetrachloronaphthalene and triphenyl phosphate.

⁸ "Celluloid" was the name applied by Hyatt to his product. Thorpe, "Dictionary of Applied Chemistry," Revised Edition **1912**, I, 705, gives brief sketch of manufacture and typical composition of celluloid.

cent (of the weight of the celluloid) remains behind and can be removed only with difficulty, *i. e.*, by extraction with certain solvents, or by saponification of the nitrocellulose. The usual composition of celluloid is 30 to 40 parts of camphor to 100 parts of nitrocellulose. If the general formula of nitrocellulose is accepted as



the nitrocellulose used for celluloid manufacture is chiefly a mixture of the hexanitrate $C_{24}H_{34}O_{20}(NO_2)_6$ (9.13 per cent N), heptanitrate $C_{24}H_{33}O_{20}(NO_2)_7$ (10.18 per cent N), and octonitrate $C_{24}H_{32}O_{20}(NO_2)_8$ (11.11 per cent N), the mixture varying from 9.5 per cent to 11 per cent in nitrogen content.

Opaque celluloid usually contains mineral matter, zinc oxide being used commonly when a white or "ivory" celluloid is desired.

PROPERTIES—The most widely accepted belief is that celluloid is a solid colloidal solution.¹ Its properties are very remarkable. It begins to soften at 80° to 90° C.² and can be shaped and molded at a somewhat higher temperature; the rigidity returns on cooling. It comes from the mold clean and retains its shape and appearance almost indefinitely. It may be colored very readily either by pigments or dyes, and suitable mechanical treatment can develop strength and color effects of remarkable beauty, ranging from brilliant, uniform, translucent shades to the finest effects in imitation of onyx, agate, and tortoise shell; or the product can be made transparent and almost colorless, or of opaque ivory whiteness.

DISADVANTAGES—Drawbacks to the use of celluloid have been previously mentioned, its price, inflammability, and odor. Its rather easy inflammability has prevented its use in certain limited fields, but has left its usefulness largely undiminished, as is evidenced by the fact that noninflammable substitutes have not replaced celluloid to any great extent. The odor, while unpleasant to many people, is not a serious drawback, although an odorless celluloid would undoubtedly possess certain advantages. The melting point of camphor is a more serious drawback in the manufacture of celluloid than is generally understood. Much confusion of thought exists on the subject.³ One compiler⁴ contradicts himself by considering the high melting point an advantage and then a disadvantage.

The high melting point of camphor does necessitate a high molding temperature (if a hard, low-camphor celluloid is to be manufactured), and this makes it necessary to exercise the greatest care to prevent discoloration of the ivory and transparent colorless grades of celluloid. It is most important to note that the generally recognized good qualities of camphor, its high solvent power for nitrocellulose, its comparative chemical stability, its colorlessness and freedom from poisonous effects on the workers, are the very foundations of the celluloid industry, and that any satisfactory camphor substitute must duplicate these desirable qualities.

¹ H. Schwarz, *Kolloidchem. Beihefte*, 6 (1914), 90; *Z. Chem. Ind. Kolloide*, 12 (1913), 32.

² Plasticity has been noted at as low as 65° C. Celluloid is very plastic at 125° C. It loses color and transparency at 140° C., and begins to decompose with evolution of gas at 145° C.

³ Auerbach, *Gummi-Ztg.*, 21 Suppl. (Jan. 25, 1906), 33, considers the high melting point of camphor an advantage.

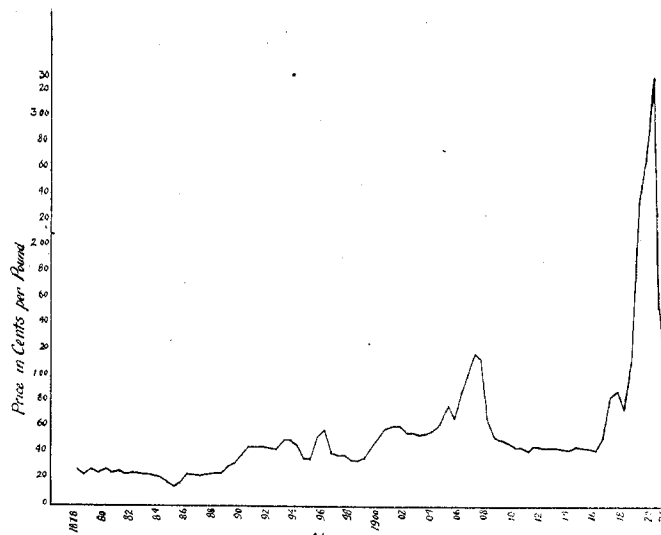
⁴ The writers too frequently ride a hobby and attempt to plead a case. Worden, "Nitrocellulose Industry," 249 (of course, W. is only quoting the literature and not giving his own opinion), in listing the advantageous properties of camphor says: "3. It has a high melting point (175°).... and therefore gives a solid celluloid, but temperature of liquefaction is not so high as to cause incipient decomposition of the celluloid." A few pages further, p. 257: "The principal objection to the use of camphor is its high melting point, which is above the decomposition point of pyroxylin. So much heat is required to mold the camphor-pyroxylin compound that there is always a tendency to discoloration and increased liability to decomposition."

THE PRICE OF CAMPHOR

A really serious drawback has been the controlling influence of the price of camphor. The price of camphor since 1878 (the earliest date available to the authors) on the dates specified is given in the table,¹ in cents per pound for American refined camphor in New York City:

	Jan. 1	July 1		Jan. 1	July 1
1878	0.28	0.24	1900	0.51	0.59½
1879	0.27½	0.25	1901	0.60½	0.60½
1880	0.28	0.25	1902	0.57	0.57
1881	0.26	0.23½	1903	0.54½	0.55½
1882	0.24½	0.23½	1904	0.58½	0.62
1883	0.23	0.22½	1905	0.78	0.68
1884	0.21	0.18	1906	0.88	1.00
1885	0.16	0.18	1907	1.17	1.14
1886	0.23	0.23	1908	0.68	0.52
1887	0.22	0.23	1909	0.50	0.48
1888	0.24	0.25	1910	0.45	0.45
1889	0.30	0.32	1911	0.42	0.46½
1890	0.39	0.45	1912	0.44	0.44
1891	0.45	0.45	1913	0.44	0.42½
1892	0.43	0.42	1914	0.42½	0.44½
1893	0.50	0.50	1915	0.44½	0.43
1894	0.45	0.37	1916	0.42	0.52
1895	0.36	0.53	1917	0.86½	0.89½
1896	0.59	0.40	1918	0.76½	1.11½
1897	0.39	0.39	1919	2.35	2.65
1898	0.35½	0.34½	1920	3.30	1.65
1899	0.37½	0.44½	1921	1.00

The accompanying graph brings out the wide fluctuations, the sudden rises and declines in the price of camphor more clearly.



CAMPHOR PRICE FLUCTUATIONS 1878-1921

THE JAPANESE CAMPHOR MONOPOLY—The successful production of synthetic camphor or the production of plantation camphor would tend to stabilize camphor prices, but the Japanese camphor monopoly has been able to prevent either form of competition from becoming strong by suitable price adjustments at the critical times, thus making it a hazardous attempt financially to go into the production of synthetic or plantation camphor. The monopoly has recently decided to refine all its camphor and to export no crude camphor. This places the celluloid industry of the world, which has already for so long labored under the disadvantage of fluctuating camphor prices, under the further danger of having its camphor supply cut off entirely whenever the Japanese celluloid industry is sufficiently advanced to warrant such a step. This opinion is confirmed by the reports that the Chinese crude camphor supply, which seemed to offer relief to celluloid manufacturers, is passing into the control of the Japanese monopoly.

CAMPHOR SUBSTITUTES

Various substitutes for camphor have been proposed and their use protected by patent grants. Many of them are obviously useless because they are more expensive even than

¹ *Oil, Paint Drug Rep.*, 1878 to 1920.

camphor. Others are colored; some produce a celluloid which is explosive; still others liberate acid which makes the celluloid unstable, and, finally, some of the substitutes proposed have little or no solvent power for nitrocellulose. Although success to a certain extent has been attained, especially in the last two years, the list of failures has been so great that writers have been moved to say:

"Of the latter [camphor], however, we may affirm that, whatever be the camphor substitute employed, no product having all the properties and qualities of celluloid manufactured from nitrocellulose and camphor can be obtained."¹

"The feverish search for a camphor substitute has been less successful, though large classes of solid solvents of pyroxylin were discovered. A few of them, belonging to the group of acid derivatives of aromatic amines, find a limited application for special purposes."²

"It is otherwise with camphor substitutes, which, called into life by the former high prices of camphor, played a not unimportant role for several years. They have since been avoided as they are easily prone to hydrolysis, or to oxidation, or to the liberation of acids which are detrimental to the nitrocellulose, the decomposition of which they induce or accelerate. By camphor substitute is meant a material which, though it does not possess all the properties of camphor, yet resembles it to the extent that it gives a solid solution with nitrocellulose, which softens on warming and becomes plastic, and is less inflammable than nitrocellulose. The number of such substitutes is legion. The author from his own experience has determined the worthlessness and even danger of the entire group of substitutes."³

RECENT SUCCESS IN MANUFACTURE—In spite of all this unfavorable evidence it is nevertheless a fact that a great measure of success has been attained with certain camphor substitutes in the United States in the last two years. One company announces in an article, "Celluloid without Camphor,"⁴ the manufacture of celluloid without natural or synthetic camphor. According to this article, the new formula eliminates both odor and taste and "reduces inflammability 50 to 80 per cent." Both in the sheet or raw material form and in manufactured articles of use the appearance is the same, and the transparency is greater in the translucent form. This last statement as to increased transparency made in the above-mentioned article should be accepted with reserve.

At the Sixth National Exposition of Chemical Industries held in New York City, September 1920, there was exhibited a product which proved upon analysis to be nitrocellulose colloided by a phenol-phosphoric acid compound. The many beautiful forms in solid colors and mottlings and in imitation of various rare and expensive natural products showed the success that had been attained by the manufacturer, although further evidence as to the working qualities and resistance to external influences of these products is required before complete success can be considered as having been attained. A third company has also been successful in producing celluloid, both transparent and opaque, in which the camphor is entirely replaced by camphor substitute. Three other companies, thus including all the very largest manufacturers of celluloid in the United States, have manufactured and sold celluloid in which the camphor was partly or totally replaced by camphor substitutes, although an equal degree of success was not obtained by all of them. In all cases the product is similar to the camphor product,

but there are minor differences in hardness and density, though the plasticity is approximately the same. The differences are so small that no important change is necessary at any stage of the manufacturing process, though it is to be expected that just as the various manufacturers differ even for the camphor product in the percentage of solvent, time for kneading, drying and seasoning, etc., so there will be minor changes of this nature necessitated by the introduction of a new raw material into the process.

The greatest difficulty has been that of producing "ivory." Most of the substitutes are esters, and minute traces of acids liberated from these esters, or traces of oxidation products of the substitutes have a slight action on the nitrocellulose or on the fillers used, so that occasionally a run is off-color. Proper choice of the substitute with proper conditions of colloidizing and proper fillers and opacifiers will ultimately overcome this difficulty. It is to be hoped that the criticism of celluloid manufacturers of the United States uttered in 1912 is no longer true:¹

A long experience in this and allied industries in the United States had demonstrated that the machinery and processes hitherto employed left much to be desired in the way of improvement, of which there had been practically none during twenty years. This condition was and is due, in all probability, to the mistaken policy of manufacturers in the maintenance of secrecy, as a consequence of which inventors, manufacturers of machinery, and scientists are kept in ignorance of the necessity for the application of their knowledge and energies in the progressive improvement which is necessary to the proper development of any industry.

The camphor-celluloid industry did not spring fully developed from the ground, and research and time will be necessary to develop fully the camphor-substitute celluloid industry. Low camphor prices and an adequate supply may largely remove the incentive to the use of substitutes.

SUBSTANCES USED—There is a very marked dearth of information on the results of the use of the various camphor substitutes, and, unfortunately, the patent literature is not a reliable source of knowledge. It is known, however, that pinene hydrochloride, for instance, which does gelatinize nitrocellulose continues to liberate hydrochloric acid rather easily, "souring" the celluloid, and has thereby caused explosions of celluloid. Other chloro derivatives as well as nitro compounds are similarly dangerous. Borneol acetate, but little cheaper than camphor, has only slight solvent action and a more disagreeable odor than camphor. However, the information is generally scanty, and even then is usually colored by the inventor's claims.

The substitutes chiefly used in the United States are the phosphoric esters, triphenyl phosphate and tritolyl phosphate (often called tricresyl phosphate), triacetin, ethyl acetanilide, and other substances to a lesser degree. Triphenyl phosphate and tritolyl phosphate have been successfully used as complete or as partial camphor substitutes, the others more often as partial camphor substitutes. The essentials in all of these substances are that the product when fused or in solution in a colorless solvent shall be colorless, and that the by-products resulting from the manufacture, such as phenol, cresol, hydrochloric acid, phosphoric acid, monoacetin, acetic acid, aniline, acetanilide, etc., shall be completely removed. (That this purity is essential is indicated by British Patent 16,271 (1906), specifying as camphor substitutes *specialty* purified carboxylic acid derivatives of secondary aromatic-aliphatic amines.) For instance, the impurities tenaciously retained by triphenyl phosphate are traces of acid and phenol. Yet it has been possible commercially to reduce the acidity of triphenyl phosphate to 0.001 per cent, calculated as HCl, the phenol to 0.002 per cent, and the ash content to less than 0.01 per cent. In other words, it is com-

¹ Masselon, Roberts, and Cilliard, "Celluloid," trans. by Herbert H. Hodgson, London, 1912, 1; see also F. Sproston, *J. Soc. Chem. Ind.*, **39** (1920), 352r.

² R. C. Schuppphaus, *THIS JOURNAL*, **7** (1915), 290.

³ Ullmann, "Enzyklopaedie der technischen Chemie," III, 308.

⁴ *Chem. Age (N. Y.)*, **28** (1920), 153.

¹ Axtell, *THIS JOURNAL*, **5** (1913), 38.

mercially possible to produce a camphor substitute which is more nearly a chemical individual than is commercial camphor.

It was thought for a time that only aromatic substances were suitable camphor substitutes, but, as the patent literature shows, numerous aliphatic substances possess solvent action toward nitrocellulose. Many of the substitutes proposed are acid derivatives of the amines or are esters, both of which classes of compounds may be fairly easily saponified or hydrolyzed, yielding acid products which accelerate the further splitting up of the compound and act deleteriously on the nitrocellulose. Others of the substitutes oxidize easily, also yielding acid products which are detrimental to the celluloid. Some of the substitutes are highly chlorinated derivatives which color easily and give off acid decomposition products.

It must be borne in mind that in order to be a satisfactory camphor substitute a substance need not necessarily be a nitrocellulose solvent. For instance, ethyl alcohol is not a nitrocellulose solvent, but if some camphor is dissolved in it (insufficient camphor to dissolve the nitrocellulose without alcohol) it becomes an excellent solvent for nitrocellulose. A case very much to the point is that of ether-alcohol mixtures. Neither ether nor alcohol alone is capable of dissolving nitrocellulose, but the mixture is a very efficient solvent. And so it is with other substances. Alone they may be ineffective, but in mixture with other solvents or non-solvents, or first dissolved in volatile solvents, these apparently nonsolvent substances may dissolve nitrocellulose, yielding a plastic product when the volatile solvent has been removed. It is a fact, however, borne out by experience with many substitutes, that those substitutes are best which, like camphor, are capable of dissolving nitrocellulose alone with the aid only of heat, pressure, and other mechanical treatment.

HARDNESS OF PRODUCT—Manufacturers of celluloid claim that the substitutes produce a soft celluloid. The softness or hardness of celluloid depends on the percentage of camphor or substitute in the celluloid. Camphor sublimates rather easily, so that camphor celluloid which is molded or otherwise heat-treated loses camphor from the surface, leaving a film of celluloid deficient in camphor and consequently hard. This "case-hardening" effect produced by the volatility of camphor is, of course, not obtained with substitutes which do not sublime at all. If a smaller percentage of the substitute is used so that the requisite hardness be obtained, difficulty is met in obtaining complete colloidizing. The obvious remedy is to use less substitutes than camphor to obtain the same hardness, a larger proportion of solvent, and a longer period of kneading to produce gelatinization.

CHARACTER OF MOST DESIRABLE SUBSTITUTES—The chemical properties of camphor make it almost the ideal solvent for nitrocellulose. Camphor is a saturated cyclic ketone. This means that camphor is a relatively stable compound not oxidized by air at ordinary, or at celluloid-molding, temperatures.

The most highly desirable camphor substitutes would seem to be substances similar in structure to camphor, and, indeed, Raschig¹ protects the use of cyclohexanone, a liquid (m.p.—45°C.). The boiling point, 161°C., is perhaps too low. It is the simplest six-membered cyclic saturated ketone, but it has not come into use. Ketones of a totally different kind, such as dinaphthyl ketone,² have also been proposed. Substances related to camphor have been patented, as isobornyl acetate³ and borneol.⁴

The great mass of substitutes proposed consists, however, neither of substances resembling camphor in structure, nor

of substances related to camphor, but of esters, amines, and of such various substances as naphthalene, dinitrobenzene, acetodichlorohydrin, resins, starch-formaldehyde condensation products, substituted ureas, gelatin, dioxydiphenylsulfone, etc.

TRIPHENYL AND TRITOLYL PHOSPHATE CELLULOIDS

As indicated above, of all this imposing array of substitutes only a few have attained any success at all, and of these only triphenyl phosphate and tritolyl phosphate have been very successful in the United States. It is claimed for celluloid made with phenol esters of phosphoric acid that it is superior to camphor celluloid in these respects:

- 1—It is less inflammable.
- 2—It is absolutely odorless.
- 3—It is very resistant to all external influences.
- 4—It is cheaper.

Triphenyl phosphate is a low-melting, white solid (resolidification point 49.9°C.). Tritolyl phosphate (tri-*o*-tolyl phosphate) is a viscous liquid which becomes very thick and glassy at -30°C. but does not solidify. In the liquid state both substances are colorless when pure. They are without odor or taste, nonvolatile, boil at very high temperatures, are stable towards air and water, and do not color on exposure to light if they have been properly purified. They saponify with difficulty, and in their solvent action on nitrocellulose they resemble camphor. Some workers¹ who have examined plastics of different makes containing triphenyl and tritolyl phosphates have found instances of brittleness, which they explain as due to insufficient colloidizing power of these substances on nitrocellulose. The authors' experience is that the colloidizing power of the above phosphates is approximately equal to that of camphor, but that more careful and longer continued mechanical treatment (in kneaders, on rolls, etc.) is necessary to bring out the full colloidizing action of triphenyl and tritolyl phosphates. The difficulties arising from the use of these substances as camphor substitutes have already been discussed, but the overcoming of these difficulties to a certain extent is amply evidenced by their widespread use when camphor prices rose. Their use is determined to a large measure by the price of camphor, but this is not the only factor. The camphor must be used with volatile solvents to overcome the difficulty arising from its high melting point. For the effective use of these solvents, chiefly alcohol, the nitrocellulose must be dehydrated. Alcohol would mix with the water contained in wet nitrocellulose, and the diluted alcohol is a poor solvent. Part of the volatile solvent is lost; usually none is recovered, or only at great cost. The liquid condition of tritolyl phosphate and the low melting point of triphenyl phosphate permit the use of these substitutes in the liquid condition without a solvent or with small proportions of solvent and wet nitrocellulose. These liquids are immiscible with water and displace the water from the nitrocellulose as they colloid it.² The water can then be removed in any convenient way. Furthermore, by proper choice of the camphor substitute or mixtures, a celluloid of the proper solidity can be produced which can be molded at a lower temperature than camphor celluloid.

TRIACETIN AND ETHYL ACETANILIDE

Triacetin has been used to a certain extent to replace part of the camphor of celluloid. Some manufacturers have experienced a fair degree of success with this substitute, while others have claimed that it causes blistering of the celluloid and liberates acid. It may be that some of the defects which have been found in triacetin, as in other camphor substitutes, are due to insufficient purification.

¹ U. S. Patent 900,204.

² Zühl and Eisemann, D. R. P. 122,166 (Oct. 28, 1900).

³ Claessen, D. R. P. 172,941 (April 7, 1905).

⁴ Béhal, U. S. Patent 831,028.

¹ Private communication.

² Lindsay, U. S. Patent 1,233,374 (July 17, 1917).

Ethyl acetanilide, or mannot, has also been used in the United States, but it is not very satisfactory. It produces a soft celluloid, which hardens on aging but becomes brittle. The higher cost, odor, and discoloration in sunlight are serious objections.

PATENTS COVERING CAMPHOR SUBSTITUTES

Following is a list of the patents for camphor substitutes. Most of them have evidently no value and others which may have value have never been used commercially, but all are included for the sake of completeness.

NUMBER	PATENTEE	DATE	CONTENT
U. S. Patents			
269340	Stevens	Dec. 19, 1882	Certain essential oils, esters and ethers
269341	Stevens	Dec. 19, 1882	Oil of caraway seed, hyssop, sage, tansy, cloves or wintergreen
269342	Stevens	Dec. 19, 1882	Dinitrobenzene, coumarin
269345	Stevens	Dec. 19, 1882	Fusel oil plus oil of hyssop, sage, tansy, wormseed, fennel seed, cloves, anise, cinnamon, sassafras, camomile, wintergreen, caraway seed, dill, acetal, amyl nitrate and amyl nitrite
386231	McClelland	July 12, 1887	Nonvolatile gums and resins, such as kauri gum, dammara resin, and gum dammar
410205	Schüpphaus	Sept. 3, 1889	Anthraquinone
410206	Schüpphaus	Sept. 3, 1889	Isovaleric aldehyde or its derivatives, amylidene dimethylether, amylidene diethylether
410207	Schüpphaus	Sept. 3, 1889	α -Naphthol and β -naphthol
410208	Schüpphaus	Sept. 3, 1889	Mixture of acetins
410209	Schüpphaus	Sept. 3, 1889	Palmitin and stearone
494790	Paget	Apr. 4, 1893	Distillate from sulfuric acid and two or more primary alcohols, distillate treated with an acid which will combine with the ethers or esters so formed and redistilled. Redistillate is the subject of patent
494791			
494792			
494793			
500617	Stevens and Axtell	Dec. 12, 1893	Acetanilide
517987	Stevens	Apr. 10, 1894	Acetanilide
528812	Schüpphaus	Nov. 6, 1894	Acid derivatives of aromatic amines, one H in NH_2 replaced by acid
542692	Stevens	July 16, 1895	Dinitrotoluene
543108	Stevens	July 23, 1895	Dinitrotoluene
543197	Stevens	July 23, 1895	Naphthalene (partial replacement)
551456	Stevens	Dec. 17, 1895	Methyl, ethyl, propyl, butyl, and amyl acetanilides
552209	Stevens	June 12, 1895	<i>p</i> -Nitrotoluene
552934	Stevens	Jan. 14, 1896	Camphene hydrochloride
553270	Stevens	Jan. 21, 1896	Dinitroxylenes
559823	Stevens	May 12, 1896	Product of oxidation of mixture of alcohols
559824	Stevens	May 12, 1896	Mixed benzoic esters
561624	Stevens	June 9, 1896	Mixed formic esters
564343	Stevens	July 21, 1896	Acetoxylicide
566349	Stevens	July 26, 1896	Antipyrine, tolpyrine, salipyrine, and tolisal
568104	Stevens and Axtell	Sept. 22, 1896	Carbanilates containing radicals of the monohydric monatomic fatty alcohols
568105	Stevens	Sept. 22, 1896	Citric esters of monohydric monatomic fatty alcohols and chloro and acetyl derivatives of these citric esters
568106	Stevens	Sept. 22, 1896	Urethanes or carbamates of the monohydric monatomic fatty alcohols, also benzyl carbamates, ethylidene urethane, acetyl- <i>p</i> -oxyphenylurethane and acetyl- <i>p</i> -ethoxy-phenylurethane
572134	Stevens	Dec. 1, 1896	Certain derivatives of crystalline aromatic acids, salol, betol or naphthalol, benzonaphthol, salacetol and benzoic anhydride
572135	Stevens	Dec. 1, 1896	Crystalline organic sulfur compounds such as trional or diethylsulfonemethylethylmethane, sulfobenzide or diphenylsulfone, sulfonal or diethylsulfonedimethylmethane, and sulfo-carbanilide or <i>s</i> -diphenylthiocarbamide
583516	Stevens	June 1, 1897	Crystalline halogen derivatives, and nitrohalogen derivatives of benzene, toluene, naphthalene, camphor, and phenol
583517	Stevens	June 1, 1897	Crystalline nitro derivatives of naphthalene and phenol
587096	Kennedy	July 27, 1897	Lanolin
595355	Stevens	Dec. 14, 1897	Aliphatic ketones, both symmetrical and unsymmetrical
596662	Nagel	Feb. 3, 1896	"Hydrochlorinated turpentine" or "camphene" (pinene hydrochloride)
597144	Goetter	July 22, 1896	Amyl acetate
598648	Schüpphaus	Feb. 8, 1898	Monobenzoate of glycerol, benzochlorohydrin, dichlorohydrin, dichloroacetin, benzomonooacetin, benzodiacetin, oleoacetin, oleodiacetin, dinitroacetin, mononitrodiacetin
598649	Schüpphaus	Feb. 8, 1898	Acetophenone, benzylideneacetone, benzophenone, phenylbenzylketone, oxyacetophenone, benzil, dibenzylideneacetone, trioxylbenzophenone, <i>p</i> -oxybenzophenone, oxyphenylbenzylketone, trioxylacetophenone
604181	Walker	May 17, 1898	Oils lighter than water obtained by the distillation of the tar of hardwoods
607554	Stevens	July 19, 1898	Certain crystalline derivatives of phenols or aromatic alcohols, dimethylhydroquinol, thymoquinone, thymol and benzoylguaiaacol
700471	Bernadac	May 20, 1902	Casein (alone or made plastic by borax)
700884	Zühl	May 27, 1902	Diphenyl carbonate, dicresyl carbonate and dinaphthyl carbonate
700885	Zühl	May 27, 1902	Triphenyl phosphate, tricresyl phosphate, trinaphthyl phosphate
741554	Schüpphaus	Oct. 13, 1903	Mixed ethers of the lower alcohols
758335	Schmidt	Apr. 26, 1904	Compounds of general formula $\text{R-SO}_2\text{A}$, where R means an aromatic radical or its substitution product. $\text{R-SO}_2\text{A}$ is the sulfonic derivative thereof, in which OH has been replaced by A, an aliphatic or aromatic ether residue
831028	Béhal	Sept. 18, 1906	Borneol or isoborneol
831488	Thieme	Sept. 18, 1906	Ureas in which hydrogen associated with nitrogen is substituted by organic radicals
881827	Rouxville	Mar. 10, 1908	Polymerized oil of turpentine
892899	Schraube and Laudien	July 7, 1908	Amidines derived from <i>o</i> -diamines, especially from <i>as</i> -trichlorodiaminobenzene and <i>p</i> -tetrachlorodiaminobenzene
900204	Raschig	Oct. 6, 1908	Cyclohexanone
946294	Vender	Jan. 11, 1910	Water-soluble acetins
961360	Lindsay	June 14, 1910	Benzyl benzoate
962877	Aylsworth	June 28, 1910	Halogenated fatty acids and their esters
996191	Ach	June 27, 1911	Organic cyclic oxides (oxygen, one or preferably more atoms in ring attached to two carbon atoms, which latter are not attached to oxygen outside of the ring), which may be produced by condensing aldehydes or ketones with polyhydric alcohols
1027617	Lindsay	May 28, 1912	Ethylene chlorohydrin
1027618	Lindsay	May 28, 1912	Ethylene acetochlorohydrin
1082573	Weedon	Dec. 30, 1913	Aldehyde-alcohols, especially acetaldo
1152625	Goldsmith	Sept. 7, 1915	Oils (drying and nondrying), oxidized by dilute nitric acid

NUMBER	PATENTEE	DATE	CONTENT
1158961	Beatty	Nov. 2, 1915	Dioxydiphenyldimethylmethane
1188356	Beatty	June 29, 1916	Dioxydiphenyldimethylmethane
1191801	Lehmann and Stocker	July 18, 1916	Polymers of cumarone and indene
1195040	Lederer	Aug. 15, 1916	Chloral hydrate
1200886	Schmidt	Oct. 10, 1916	Acyl compounds of completely hydrogenated amines
1309981	Clarke	July 15, 1919	Simple higher dialkyl oxalates
1354725	Carroll	Oct. 5, 1920	Mixture of tetrachloronaphthalene and triphenyl phosphate
1360759	Kessler	Nov. 30, 1920	Acetins free from monacetin and free acetic acid
German Patents			
56946	Güttler	Dec. 17, 1889	Nitrocarbohydrates (cellulose, sugar, starch, gums) are fused with solid derivatives of the hydrocarbons (dinitrobenzene and dinitrophenol)
66055	Koller	Mar. 29, 1892	A paste of nitrocellulose, sulfur, nondrying oils, and resins or their solutions in oils is heated with viscous collodion at 100°-105° in an autoclave at 12 atmospheres pressure
80776	Schüpphaus	Nov. 6, 1894	Formanilide, <i>o</i> -acetophenetidine, <i>o</i> -acetotoluidide, <i>p</i> -acetophenetidine, <i>p</i> -acetotoluidide, benzanilide, and their bromo and nitro derivatives
85235	Marga	Sept. 5, 1894	Pure cellulose or mechanical wood powder is added to an alcohol-ether solution of nitrocellulose (Celludine)
96365	Beid and Earle	Nov. 28, 1895	Nitro derivatives of oils containing linolein or ricinolein are mixed with nitrocellulose
102962	Stracke	Sept. 2, 1898	Resin soaps and finely divided resin- or bitumen-containing substances (bark, rich peat, and bituminous shales) are mixed with nitrocellulose and pressed hot
114278	Kohl	July 19, 1899	Pyroxylin and gelatin in glacial acetic acid
115681	Spitaler	July 15, 1899	Albuminoids, especially casein, freed from constituents insoluble in caustic, are dissolved in borax and distilled water, and gelatinized paste added to nitrocellulose
117542	Société Générale pour la Fabrication des Matières Plastiques	June 28, 1899	Naphthalene
118052	Zühl and Eisemann	Apr. 15, 1900	α -Naphthyl acetate or β -naphthyl acetate is treated with twice its weight of nitrocellulose in the presence of solvents (methanol)
119636	Zühl and Eisemann	July 7, 1900	Phenoxyacetic acids, naphthoxyacetic acids or their anhydrides or esters are treated with nitrocellulose
122166	Zühl and Eisemann	Oct. 28, 1900	Methylnaphthylketone, dinaphthylketone, methoxynaphthylketone or dioxynaphthylketone is treated with nitrocellulose in the usual manner
122272	Höchst	Oct. 10, 1900	Aromatic sulfonic acid derivatives which are derived from chlorides, esters, and amides; especially <i>p</i> -toluenesulfoalkyl- and -dialkylamides and other derivatives obtained in the preparation of saccharin from <i>p</i> -toluenesulfonechloride, such as <i>p</i> -toluenesulfonic acid alkyl ester, <i>p</i> -toluenesulfonic acid aliphyl ester, <i>p</i> -toluenesulfamide. For this purpose there are always used two or more bodies of the groups named
125315	Goldsmith and British Xylonite Co., Ltd.	Oct. 31, 1900	Reaction products of hydrochloric acid solution (or gas) and acetic acid and glycerol, such as acetodichlorohydrin, diacetochlorohydrin, monoacetomono-chlorohydrin, which are used alone or in mixture; for instance, to 100 parts of soluble nitrocellulose, 5 parts of camphor and 20 parts of the above-named substitutes in alcoholic solution are added
127816	Höchst	June 30, 1900	Neutral alkyl or aliphyl esters of phthalic acid
128119	Zühl and Eisemann	Mar. 10, 1901	Nitrocellulose is treated with oxanilic acid esters in which the aniline may also be replaced by homologous or substituted bases of the aromatic series
128120	Zühl and Eisemann	Mar. 21, 1901	To nitrocellulose are added phenol esters of phosphoric acid, such as triphenyl phosphate, tricresyl phosphate, trinaphthyl phosphate
128956	Zühl and Eisemann	Mar. 21, 1901	Mono- or polyhalogen substitution products of aromatic hydrocarbons, such as dichlorobenzene and monochloronaphthalene
132371	Deutsche Zelluloidfabrik	May 15, 1901	Acetyl derivatives of such secondary amines as have two hydrogen atoms of the ammonia replaced by aromatic radicals, such as acetyldiphenylamine
138783	Franquet	July 25, 1901	Casein made plastic by borax solution and then dehydrated is added to a solution of nitrocellulose
139589	Zühl and Eisemann	Sept. 30, 1900	Phenol esters of carbonic acid such as diphenyl carbonate, dicresyl carbonate, or dinaphthyl carbonate
139738	Goldsmith and British Xylonite Co., Ltd.	Dec. 14, 1901	One or more acid or neutral esters of sebacic acid; for instance, 100 parts nitrocellulose are worked up in alcoholic solution with 40 parts of the finally purified product obtained by the oxidation of castor or coconut oil by nitric acid and subsequent esterification with methanol
139905	Franquet	Feb. 23, 1902	In No. 138783 casein is replaced by caseinates
140164	Zühl and Eisemann	Oct. 27, 1901	Triphenyl, tricresyl, and trinaphthyl thiophosphates
140263	Rheinische Gummi- und Zelluloidfabrik	Jan. 14, 1902	Organic acid esters of the sugars (glucose, levulose and sucrose) such as acetochlorohydrate, glucose dibutyrate, glucose distearate, glucose ditartrate, glucose tetratrate, glucose diacetate, glucose tetraacetate, glucose pentaacetate, octacetyl glucose, penta-acetyl levulose, tetra-acetyl lactic acid, lactose tartrate sucrose mono-, tetra-, hepta- and octacetate
140480	Rheinische Gummi- und Zelluloidfabrik	Feb. 26, 1902	α - and β -Phenylnaphthalene, α - and β -dinaphthylmethane, and α - and β -benzylnaphthalene
140855	Rheinische Gummi- und Zelluloidfabrik	Jan. 14, 1902	Glucose, levulose, and lactose replace camphor, and sufficient pressure is applied to cause solution of the nitrocellulose
142452	Zühl and Eisemann	Nov. 21, 1901	Alcohol esters of phenol phosphoric acids and halogen derivatives thereof
142971	Zühl and Eisemann	May 18, 1902	Such esters as contain alcoholic groups as well as phenolic groups, such as ethyl ester of diphenyl phosphoric acid, dimethyl ester of cresyl phosphoric acid, or amyl ester of dinaphthyl phosphoric acid
142832	Zühl and Eisemann	June 16, 1902	Halogenated phenol esters of phosphoric acid, as neutral phosphoric acid esters of dichlorophenol, dichloronaphthol and tetrachloronaphthol
144648	Zühl and Eisemann	Oct. 26, 1902	Phosphoric acid derivatives in which one or two hydroxyls are replaced by phenoxy, cresoxy, or naphthoxy groups, and the remaining hydroxyls by aniline groups, such as diphenyl phosphoric acid anilide, cresyl phosphoric acid anilide or dinaphthyl phosphoric acid anilide
163668	Claessen	June 8, 1904	Low melting resins or ceresin are used with nitrocellulose completely soluble in 96 per cent alcohol; for example, 100 parts nitrocellulose are dissolved in 30 parts colophony and 60 parts 96 per cent alcohol
168497	Rheinische Gummi- und Zelluloidfabrik	July 22, 1903	Sugary or starchy products, especially dextrin, are treated with aldehydes and used as camphor substitutes, such as sugar formalin or starch formalin
172941	Claessen	Apr. 7, 1905	Isobornyl acetate
172966	Claessen	June 22, 1904	Benzylidene acetoacetic ester, or benzylidene diacetoacetic ester in mixture with each other
172967	Claessen	July 2, 1904	The above-named acetates in mixture with product obtained by the action of HCl on these substances, 3-methyl-5-phenyl-4,6-dicarboxethyl-d ₂ -keto-R-hexene
173020	Bad. Anil. Soda Fab.	Dec. 16, 1904	Benzylidene diacetate or its monochloro substitution products
173796	Zühl and Eisemann	Sept. 22, 1905	Phosphoric acid esters of dichlorohydrin
174259	Claessen	Oct. 29, 1904	Nitrocellulose is dissolved in ethylidene diacetoacetic ester or in the mixture of it with benzylidene acetoacetic esters

NUMBER	PATENTEE	DATE	CONTENT
174914	Raschig	July 16, 1905	Cyclohexanone, cyclohexanol, as well as their homologs, alone or in mixture
176474	Bad. Anil. Soda Fab.	July 26, 1905	Alkylaceto compounds of tri- and more highly chlorinated anilines in which both o-positions to the amino group are occupied by chlorine, with the exception of s-methylacetotetrachloroanilide and benzylacetopentachloroanilide
177778	Zühl and Eisemann	Nov. 18, 1904	Together with the camphor substitutes in D. R. P. 128956 and 139589 there should be added as "hardening" material such substances as resins or resinous bodies; for example, shellac, dammar, mastic, acaroid resin, colophony, resin-acid esters; for many purposes also hard resins such as copal and amber
178133	Claessen	Mar. 11, 1906	Substitution products of urea in which all the hydrogen bound to nitrogen is replaced by organic radicals
180126	Bad. Anil. Soda Fab.	Apr. 21, 1906	Amidines derived from o-diamines
180208	Bad. Anil. Soda Fab.	Aug. 9, 1905	s-Methylbenzoyltrichloroanilide
191454	Claessen	Aug. 23, 1906	Ureas or thioureas in which all the hydrogen atoms are replaced by organic radicals or their halogen derivatives
185808	Basler & Co.	June 7, 1905	Borneol or isoborneol alone or with admixture of some camphor in the presence of a solvent (ethyl acetate, amyl acetate, acetone) which is later removed
188822	Rheinische Gummi- und Zelluloidfabrik	Nov. 9, 1905	Condensation products, which result from the action of formaldehyde on terpenes, terpene-containing ethereal oils, resins, and balsams
202720	Szelinski	Dec. 28, 1907	The products of the action of organomagnesium compounds on hydroaromatic ketones such as carvone, pulegone, and cyclohexenone
207869	Desvaux and Allaire	Apr. 17, 1908	Camphor is partly replaced by the albuminoid substance obtained from maize according to D. R. P. 144217
214193	Herstein	Nov. 23, 1907	Nitrocellulose treated with caustic alkali and hardened by weak acids and salts
214398	Buchstab	July 23, 1908	Pass air through nitrocellulose solution, then add lactic acid and strontium chloride and castor oil
214962	Boehringer and Sons	Dec. 5, 1906	Cyclic ethers which are prepared by condensation on one hand from aldehydes and ketones, and on the other hand from polyatomic alcohols of the formula $\text{CH}_2\text{OH}(\text{CHOH})_x\text{CH}_2\text{OH}$
219918	Chemische Fabrik Griesheim-Elektron	July 9, 1908	Dioxydiphenylsulfone
220228	Lederer	Feb. 24, 1907	Chloral hydrate, chloral alcoholate, etc.
221081	Soc. Indust. de Celluloid	Jan. 13, 1909	Maltodextrin neutralized with borax added to nitrocellulose-camphor (or camphor-substitute) mixtures
242467	Berend	July 16, 1908	Nitrocellulose dissolved with anhydroformaldehyde compounds of resin, oil or fatty acids and primary amines in acetone, the solution emulsified with gelatin, casein, or albumin solution, and the emulsion hardened by formaldehyde
240046	Danzer	June 23, 1910	Nitrated cellulose sheets treated with solvent for nitrocellulose
251372	Celluloid Co.	June 7, 1910	Benzyl benzoate in the presence of solvents
281225	Bad. Anil. Soda Fab.	Nov. 29, 1913	Acyl derivatives of completely hydrogenated aromatic amines (acetyldicyclohexylamine obtained by acetylation of dicyclohexylamine)
292951	du Pont de Nemours	Oct. 10, 1912	Aldehyde-alcohols, like acetaldol
319723	Clouth	Dec. 6, 1917	Cellulose esters either alone or with "softening" materials soluble in anthracene oil are mixed with anthracene oil
			French Patents
254695	Nagel	Mar. 12, 1896	Pinene hydrochloride or "camphene"
292983	Société Générale pour la Fabrication des Matières Plastiques	Oct. 2, 1899	Naphthalene
295592	Cie. Paris de Couleurs d'Anilin	Dec. 23, 1899	Alkyl ethers of aromatic sulfonic acids, especially of p-toluenesulfonic acid, p-toluenesulfamide and p-toluenedialkylamide
300676	Marx and Destaux	May 26, 1900	Nitronaphthalene
308372	Zühl	Feb. 22, 1901	Phthalic acid, o-phthalic anhydride, phthalonic acid, benzene tricarboxylic acid, and their esters
309962	Zühl	Apr. 15, 1901	Triphenyl, tricresyl, trinaphthyl phosphates; substituted products of triphenyl, tricresyl, and trinaphthyl phosphates, substituted in rings or with oxygen of $\text{P}=\text{O}$ replaced by sulfur
Addition 148 of Feb. 22, 1902 to 309962			
312817	Franquet	July 18, 1901	Acetyldiphenylamine, triphenyl phosphate, amyridine dimethyl and diethyl esters
319926	Soc. Ind. de Cellulose	Nov. 27, 1902	Gelatin or an ammoniacal solution of gelatin
320133	Soc. Anon. l'Oyonnaxienne	Apr. 2, 1902	Camphor partly replaced by gelatin and the product hardened by formaldehyde
322506	Callenberg	June 27, 1902	Halogenated ethereal oils, especially chlorinated turpentine
331819	Soc. Anon. l'Oyonnaxienne	Oct. 3, 1903	Camphor partly replaced by albumin; hardened by formaldehyde
339081	Proveux	Oct. 5, 1903	Nitrocellulose plus camphor and casein or casein alone combined with glycerol and boric acid (Caséilithe)
340266	Schmerber	Feb. 8, 1904	Methylacetanilide
341556	Weiler-ter-Meer	Mar. 23, 1904	Mono- and polyhalogen derivatives of primary amines; acyl derivatives of halogenated primary amines and acyl derivatives of secondary aromatic-aliphatic amines
349970	Béhal, Magnier and Tissier	June 7, 1904	Borneols
352853	Gillet	Mar. 30, 1905	20-50 per cent camphor replaced by rosin or other resin of equal solubility in alcohol
362090	Claessen	Feb. 8, 1906	Benzylidene diacetylacetic ester and benzylidene acetylacetic ester
363846	Bad. Anil. Soda Fab.	Mar. 5, 1906	Alkyl-acyl derivatives of polychloroanilines containing three or more chlorine atoms, two of which are ortho to the amino group
364604	Claessen	Mar. 26, 1906	Ureas with the four hydrogen atoms attached to nitrogen replaced by organic radicals
365297	Bad. Anil. Soda Fab.	Apr. 14, 1906	Acyl derivatives of monoalkylanilines thrice or more halogenated in which two positions ortho to the amino group are occupied by halogen
366106	Bad. Anil. Soda Fab.	May 11, 1906	Amidines derived from aromatic o-diamines; amidines containing two atoms of chlorine ortho to the nitrogen atoms
372018	Mestrallet-Petry	Dec. 1, 1906	Gelatin
372512	Arbez-Carme	Dec. 14, 1906	Mixture of rosin and naphthalene
372599	Bondet	Dec. 15, 1906	Gelatin, glucose, resinous matters, and vegetable oil added to celluloid to make a plastic product
374395	Peyrusson	Apr. 14, 1906	Ricinates or ricinoleates of metals, especially Mg, Zn, Pb, Al, with or without chlorides of Zn, Mg, Mn, or Cu
Addition 8760 to 374395	Peyrusson	Apr. 13, 1907	Sulfuricnates are equivalent to ricinates of original patent
376269	Rouxville	June 5, 1906	Certain hydrocarbons prepared according to French Patent 356916 of Aug. 7, 1905
377010	Lederer	Apr. 20, 1907	Chloral hydrate; chloral alcoholate
377671	Weiler-ter-Meer	July 17, 1906	Acyl derivatives of secondary aliphatic aromatic amines, specially purified
382270	Gillet	Dec. 3, 1906	Rosin and castor oil
382350	Gillet	Dec. 5, 1906	Rosin and castor oil varied according to hardness desired
383478	Dubosc	June 9, 1908	Borneol esters

NUMBER	PATENTEE	DATE	CONTENT
387179	Soc. Anon. Nouvelle "L'Oyonnithe"	Feb. 12, 1908	Aliphatic esters of fatty acids derived from fats, such as palmitic, stearic, oleic, ricinoleic and linoleic
387537	Assadas	May 8, 1907	Noninflammable plastic of nitrocellulose using hypophosphorous acid or its barium salt, neutralizing free acidity by means of specified sulfur compounds, and replacing camphor by colophony
404028	Commercial Products Co.	April 14, 1909	Gelatin with or without casein and albumin in phenol or anhydrous glycerol is treated with paraformaldehyde in anhydrous glycerol, added to nitrocellulose colloided by anhydroformaldehydeaniline or the resinates of the latter
409557	Bretaeau and Leroux	Feb. 19, 1909	Aromatic aldehydes and similar alkylated or acylated derivatives; hydroaromatic ketones such as hexahydrobenzylketone, hydronaphthylketones
432264	Dreyfus	July 15, 1911	(a) Mono- or polyhalogenated derivatives of benzene, toluene, and naphthalene and side-chain derivatives, halogenated in lateral chain or nucleus, or both (b) Nitro derivatives of benzene, toluene, and naphthalene (c) Ethers of mono- or polyphenols (d) Halogenated camphor (e) Ketones (f) Side-chain aromatic alcohols (g) Mixtures of above
Addition 16854 to 432264	Dreyfus	Nov. 19, 1912	Instead of substances named in principal patent, products obtained by the action of metal phenolates or alcoholates on chlorinated aliphatic compounds
447645	Beatty	Aug. 26, 1912	s-Dihydroxydiphenyldimethylmethane and amyl acetate
449606	du Pont de Nemours	Oct. 19, 1912	Aldols, preferably nonvolatile and polymerizable, such as acetaldo
449607	du Pont de Nemours	Oct. 19, 1912	Acetaldo
452432	LeCamphre	Mar. 6, 1912	Halogen derivatives of camphor
465345	Nouvelle L'Oyonnithe	Nov. 26, 1913	To nitrocellulose and camphor add 50 to 70 per cent of castor oil; the castor oil can be partially replaced by acetin or mannol For triformin, epiformin, etc., see G. Moyer, <i>Caoutchouc gutta-percha</i> , 10 (1913), 7386 For amyl and butyl ricinoleates and tartrates, see Djeinem, <i>Caoutchouc gutta-percha</i> , 17 (1920), 10402 For alkyl esters of higher fatty acids (like ethyl ricinoleate), see Luttringer, <i>Bull. Soc. Ind. Rouen</i> , 48 (1920), 81 ¹
British Patents			
7277	Paget	Apr. 8, 1893	Mixed ethers, such as ethylamyl ether
7784	Paget	Apr. 17, 1893	Distillate from sulfuric acid and two or more primary alcohols, distillate treated with an acid which will combine with the ethers or esters so formed and redistilled. Redistillate is the subject of patent
22137	Paget	Nov. 18, 1893	Various ozonized solvents
21331	Schüpphaus	Nov. 6, 1894	Alkyl derivatives of aromatic amines and their substitution products
13287	Chaubet	June 27, 1899	Naphthalene
15355	Höchst	July 26, 1899	1.8 parts nitrocellulose dissolved in 16 parts glacial acetic acid, with 5 parts gelatin added
25434	Höchst	Dec. 22, 1899	Compounds of general formula R-SO ₂ A, where R means an aromatic radical or its substitution product. R-SO ₂ A is the sulfonic derivative thereof in which, OH has been replaced by A, an aliphatic or aromatic ether residue
13131	Goldsmith and British Xylonite Co.	July 20, 1900	Acetochlorohydrins, acetins, benzicins, esters of phthalic acid and anhydride, and esters of succinic acid, pulegone, thujone, or oils containing these, and condensation products of acetone or acetone oils with benzaldehyde, acetaldehyde, or formaldehyde
17948	Zühl	Oct. 9, 1900	Esters of phenols or derivatives with mono- or polybasic aliphatic acids, as diphenyl carbonate, naphthol propionate, resorcinol diacetate, and others
20733	Zühl	Nov. 16, 1900	Solid ketones such as methylnaphthylketone, dinaphthylketone, methyloxynaphthylketone, dioxynaphthylketone
4326	Zühl	Feb. 28, 1901	Esters and anhydrides of phthalic and phthalonic acids
8063	Bonnaud	Apr. 19, 1901	Nitrocellulose in alcohol and camphor. Add gum copal in boiling castor oil, and mineral matters
8072	Zühl	Apr. 19, 1901	Phosphoric esters of phenols, and naphthols
10213	Zühl	May 16, 1901	Halogen derivatives such as trichlorobenzene, dichloronaphthalene, trichloronitronaphthalene, trichloroaniline
22662	Goldsmith and British Xylonite Co.	Nov. 9, 1901	Alkyl esters of acids obtained by oxidizing fats and soaps, including alkyl esters of oxalic acid series. Acetylated and benzoylated secondary aromatic amines. Alkyl esters of lactic and tartaric acids and their acetyl and benzoyl derivatives
9416	Edeleanu and Filiti	Apr. 23, 1902	Nitrated petroleum products
4383	Zühl	Feb. 20, 1902	Substituted products of triphenyl, tricesyl, and trinaphthyl phosphates, substituted in the rings, or with oxygen of $\equiv P=O$ replaced by sulfur
23445	Zühl	Oct. 27, 1902	Phosphoric acid derivatives of the type $O=P \begin{matrix} \nearrow OR_1 \\ \searrow A \end{matrix} OR_2$ where OR ₁ and OR ₂ are phenoxy, cresoxy, or naphthoxy residues, and A represents an ester or anilide group
3045	Ensminger	Feb. 9, 1903	Nitrocellulose, casein and camphor plastic is decamphorated and hardened by formaldehyde
23752	Casein Co. of America	Nov. 2, 1903	Add casein dissolved in glacial acetic acid to nitrocellulose
5280	Ortmann	Mar. 3, 1904	Ketones such as methylethyl, methylnaphthyl, dinaphthyl, methoxynaphthyl, dioxynaphthyl, together with turpentine and naphthalene
9277	Woodward	Apr. 22, 1904	Noninflammable celluloid produced by mixing fish glue, gum arabic, gelatin, and rape oil with celluloid
15435	Weiler-ter-Meer	July 11, 1904	Mono- or polyhalogen derivatives of primary amines and their acyl compounds. Acid derivatives of secondary amines which contain an aromatic or aliphatic radical
11512	Béhal	June 1, 1905	Borneol and isborneol
2817	Weiler-ter-Meer	Feb. 5, 1906 (void)	Acyl derivatives of secondary aromatic-aliphatic amines, specially purified
8077	Bad. Anil. Soda Fab.	Apr. 3, 1906	Alkyl-acyl derivatives of polychloroanilines, containing three or more chlorine atoms, two of which are ortho to the amino group
10228	Bad. Anil. Soda Fab.	May 1, 1906	Polychloroamidines and alkyl derivatives thereof (from <i>as</i> -trichlorodiaminobenzene and <i>v</i> -tetrachlorodiaminobenzene)
10228A	Bad. Anil. Soda Fab.	May 1, 1906	Amidines from <i>o</i> -diamines, and especially those produced in 10228
16271	Weiler-ter-Meer	July 18, 1906	Specially purified carboxylic acid derivatives of secondary aromatic-aliphatic amines
20037	Claessen	Sept. 8, 1906	Ureas in which the four hydrogens of the ammonia residues are substituted by organic radicals
9537	Lederer	Apr. 24, 1907	Chloral hydrate and chloral alcoholate
11397	Bethisy, Fouchard and Vignes	May 15, 1907	Bleached tetranitrocellulose with 40 to 45 per cent water content is saturated with 5 per cent liquid hydrocarbon and then treated with mixture of acetic acid, sulfuric ether, acetone, amyl acetate, and solution of <i>unona selanica</i>
21880	Self-Developing Plate Co. and Bolas	Oct. 3, 1907	Gelatinizing nitrocellulose sheet without camphor, but merely with alcohol and pressure without dissolving nitrocellulose

NUMBER	PATENTEE	DATE	CONTENT
8542	Briailles	Apr. 16, 1908	Gelatin and nitrocellulose, oil of acetone, and vaseline oil as celluloid substitute
15855	Griesheim-Elektron	July 7, 1909	Dioxydiphenylsulfone
20975	Dreyfus	Sept. 22, 1911	1—Alcoholic or phenolic ethers of mono- or polyphenols and their homologs 2—Aromatic side-chain alcohols and their substitution products
3869	Bad. Anil. Soda Fab.	Feb. 15, 1912 (void)	Lower fatty acid esters of cyclohexanol, cyclopentanol, and their homologs
18822	Beatty	Aug. 16, 1912	Dioxydiphenyldimethylmethane
22623	du Pont de Nemours	Oct. 4, 1912	(Nitrostarch or nitrocellulose), monomolecular aldols such as acetaldol
18499	Beatty	June 19, 1913	Dioxydiphenyldimethylmethane
9270	Bad. Anil. Soda Fab.	Apr. 14, 1914	Acy derivatives of completely hydrogenated aromatic bases

The Catalytic Oxidation of Petroleum Oils^{1,2}

By C. E. Waters

BUREAU OF STANDARDS, WASHINGTON, D. C.

Earlier papers from this Bureau have dealt with the oxidation of petroleum oils, chiefly in connection with a so-called carbonization test for automobile lubricating oils.³ The idea upon which the test is based is the partial oxidation of the oil, followed by polymerization of the oxidation products to asphaltic matter.

Many oil chemists do not accept this idea, but think that the so-called carbon deposits in the engine are the result of cracking of the lubricant.⁴ Be that as it may, there is no doubt that petroleum oils are rather easily oxidizable under certain conditions and yield precipitates when diluted with petroleum ether. Those who claim that cracking is the chief cause of the formation of the deposits in engines seem willing to accept the statement that oxidation of transformer oils causes sludging. It is also believed that oxidation causes the deterioration of turbine oils.

For a number of years transformer oils have been tested by subjecting them to oxidation or by determining their content of unsaturated hydrocarbons, which may be expected to become oxidized when the oil is in use.

The idea that the deterioration of turbine oils is due to oxidation seems to be a more recent one. Perhaps the next step will be for those who would then be called extremists to say that nearly all lubricants should be subjected to an oxidation test, because all except steam cylinder oils are used in contact with air.

The commonest method for testing transformer oils was devised by Kissling.⁵ The oil is kept at 150° C. for 50 hrs. while oxygen is slowly bubbled through it. Sometimes a piece of copper gauze is placed around the delivery tube to act as a catalyst. Modifications of the procedure require heating for as long as 72 hrs. The oxidized oil is first extracted with alcoholic soda, and then the asphaltic matter is precipitated by the addition of petroleum ether. The results are called the "resinification constants," or the "tar-forming" and "coke-forming" numbers.

Nastjukoff's "formolite" reaction⁶ is sometimes used to determine the quality of transformer oils. By treatment with formaldehyde and concentrated sulfuric acid, insoluble condensation products are formed from the unsaturated cyclic and alicyclic hydrocarbons. The paraffins, naphthenes, and some other series do not react. The olefins are un-

saturated, but do not react, or at least do not yield insoluble products. It does not necessarily follow that they do not take part in the formation of sludge.

EFFECT OF METALS ON OXIDATION OF PETROLEUM OILS

There are many cases in which metals or their compounds are used as catalysts for accelerating oxidation, hydrogenation, and similar operations in organic synthesis. It seemed desirable to learn whether the presence of various metals or their oxides would affect the rate of oxidation of petroleum oils. A few data on this subject, which were presented some years ago, were inconclusive, but they at least indicated that brass accelerates the oxidation. Besides brass, tubes were made of glass, high and low carbon steel, cast iron, vanadium steel, and chrome-vanadium steel. The oil was heated in these tubes.¹ Unfortunately, they had to be made so small that the surface of oil exposed to oxidation was not sufficiently great.

Other results, obtained by heating oil in flasks of the usual size, showed the effect of the presence of fatty oils, sulfur, asphalt, rosin and rosin oil, soap, and ferric oxide.² It has also been found that when oil has first been partly oxidized by exposure to air and sunlight,³ or when the varnish-like coating formed inside of the flask during a previous test is not removed, the amount of asphaltic matter produced by heating is increased. Still more recently it has been found that organic sulfur compounds which do not darken polished copper seem to increase the rate of oxidation.⁴

EXPERIMENTAL METHOD

In the experiments, the results of which are given below, strips of sheet metal 11 by 72 mm., and from 0.2 to 0.6 mm. thick, were placed diagonally inside of the 150-cc. flasks in which the oils were heated. The strips were thus surrounded by a mixture of oil vapors and air. As the vapors tend to be acid, some of the metal was expected to dissolve and be washed down into the oil.

Most of the strips were polished with fine emery paper, washed with water, and wiped dry. Other strips after polishing were coated with oxide by gentle heating over a low flame. Still others were covered with sulfide by leaving them over night in a glass-stoppered bottle into which hydrogen sulfide had been passed for a few moments. Finally, a few tests were made with strips which still had clinging to them the varnish-like coating of oxidized oil from a previous determination.

¹ Presented before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 28 to 29, 1921.

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³ Waters: Bureau of Standards, *Scientific Papers* 153 and 160; *Technologic Papers* 4 and 73; *Circular* 99. See also *THIS JOURNAL*, 2 (1910), 451; 3 (1911), 233, 812; 8 (1916), 587.

⁴ See discussion in *Circular* 99.

⁵ *Chem.-Ztg.*, 30 (1906), 932; 31 (1907), 328; 32 (1908), 938; 33 (1909), 521.

⁶ Nastjukoff, *Petroleum*, 4 (1909), 1336, 1397; Severin, *Ibid.*, 6 (1911), 197; Heer, *Chem.-Ztg.*, 34 (1910), 893; Marcusson, *Ibid.*, 35 (1911), 729.

¹ Bureau of Standards, *Scientific Paper* 160 (1910), 373; *THIS JOURNAL*, 3 (1911), 233.

² Bureau of Standards, *Technologic Paper* 4 (1911); *THIS JOURNAL*, 3 (1911), 812.

³ Bureau of Standards, *Technologic Paper* 73 (1916); *THIS JOURNAL*, 8 (1916), 587.

⁴ Bureau of Standards, *Technologic Paper* 177 (1920), 8; *Circular* 99 (1920), 13.