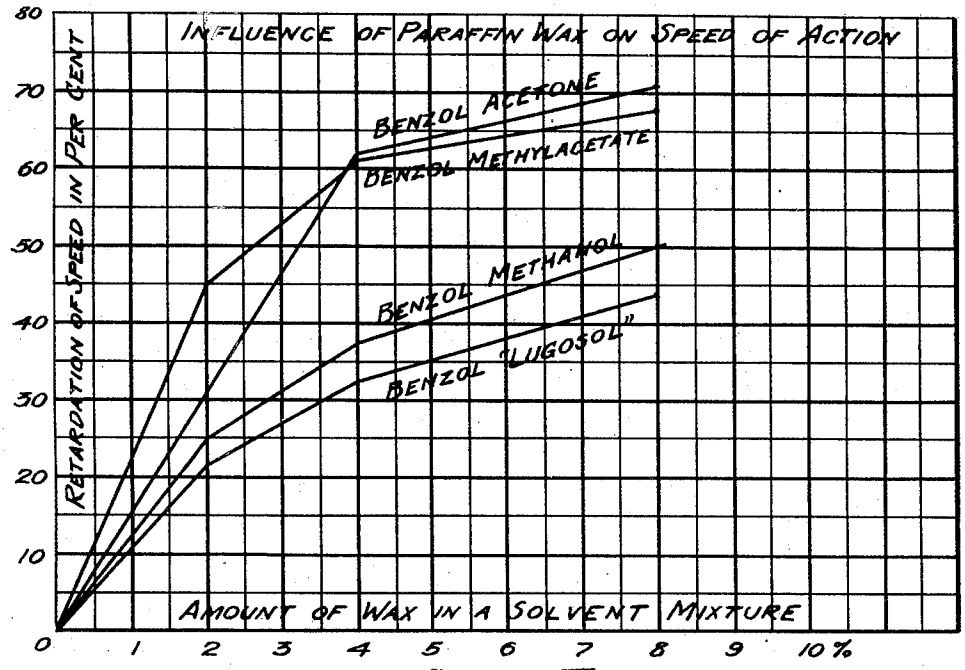
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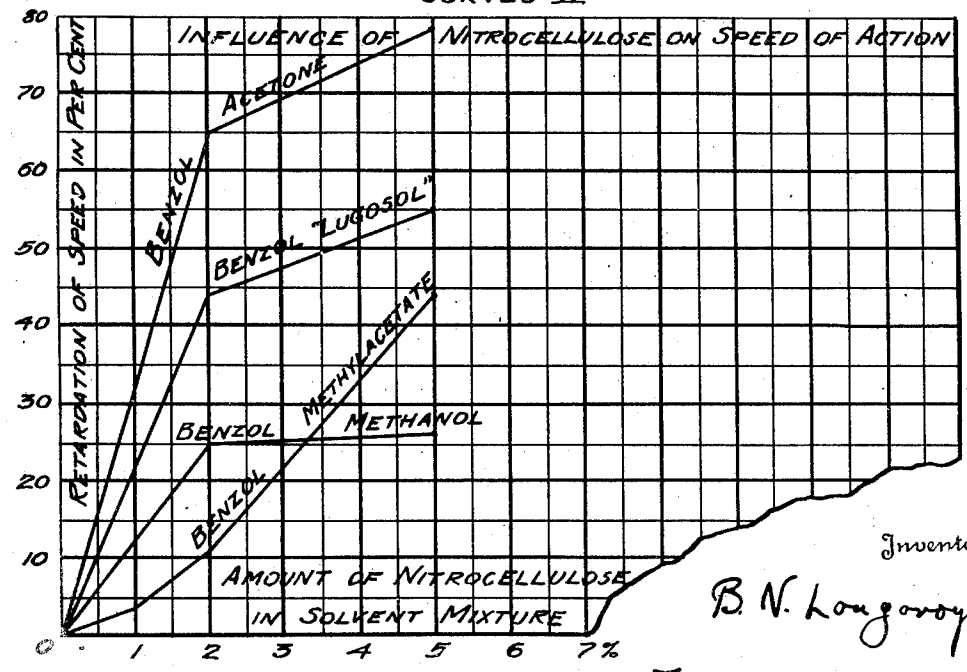
PAINT AND VARNISH REMOVER CONTAINING KETONE CONDENSATION SOLVENTS

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CURVES I



CURVES II



Inventor

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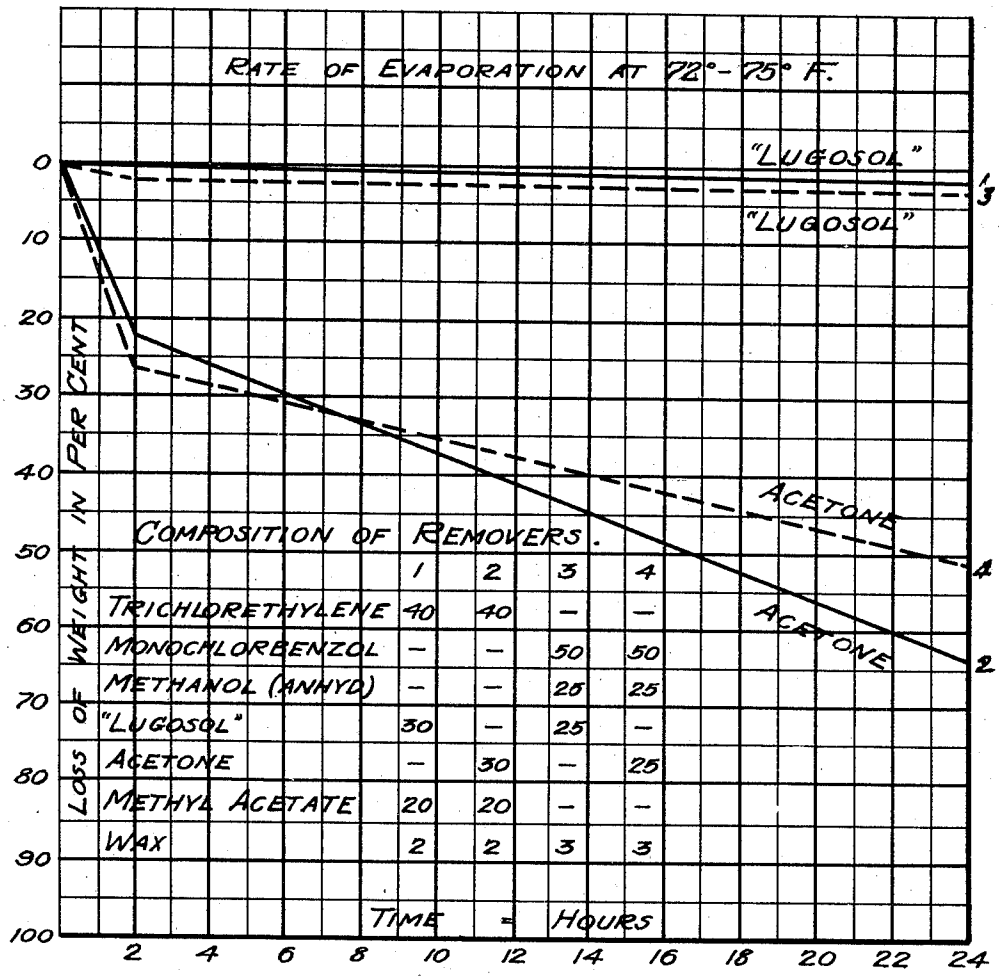
By Foster & Codier Attorneys

Oct. 25, 1932. B. N. LOUGOVOY 1,884,765

PAINT AND VARNISH REMOVER CONTAINING KETONE CONDENSATION SOLVENTS

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CURVES III



COMPOSITION OF REMOVERS.

	1	2	3	4
TRICHLORETHYLENE	40	40	—	—
MONOCHLORBENZOL	—	—	50	50
METHANOL (ANHYD)	—	—	25	25
"LUGOSOL"	30	—	25	—
ACETONE	—	30	—	25
METHYL ACETATE	20	20	—	—
WAX	2	2	3	3

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Patented Oct. 25, 1932 1,884,765

UNITED STATES PATENT OFFICE

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PAINT AND VARNISH REMOVER CONTAINING KETONE CONDENSATION SOLVENTS

Application filed May 26, 1928. Serial No. 280,955.

This invention relates to a finish remover comprising ketonic condensation solvents and has for its object the production of a composition adapted for the removal of the finish from painted or varnished surfaces, or broadly from surfaces carrying a dried finish coating which it is desired to remove.

A useful paint and varnish remover already known is made with benzol and acetone in suitable proportions, carrying three or four ounces of paraffin wax per gallon.

The activity of a paint and varnish remover is usually tested in the trade by a method which is not absolutely scientific but nevertheless is regarded sufficiently convincing to the user. This method involves the application of some of the removing composition to a surface coated with a paint or varnish and noting the time taken for the surface to wrinkle. The time necessary for producing this wrinkling effect is regarded as inversely proportional to the solvent action or "cutting power" of the removing composition.

While this might be sufficient for ordinary testing by the customer, a more exact method of determination of comparative cutting power would be desirable in rating the removing action of various solvents.

The method adopted when working on the present problem was as follows: A piece of old painted wood was selected, taking care that the portion used had a good even, thick coat of paint, and this was cut into strips. Various solvents were placed in a series of test tubes and a strip of the painted wood was put into each test tube. The time which elapsed before the first appearance of any wrinkling was noted accurately for each solvent by means of a stop watch. The comparative "removing action" was thus roughly represented by the number of seconds.

Solvent mixtures vary greatly in cutting power. In removers involving the use of a penetrating hydrocarbon, such as benzol, and a loosening solvent of an alcoholic or ketonic nature, a very great variation is observable in the cutting action depending upon the choice of solvents. Practically speaking, benzol is the most active and cheapest penetrating hydrocarbon. Acetone is a readily available and highly effective ketone body which is being used in paint and varnish removers at the present time.

In the course of my work along the line of paint and varnish remover, I discovered that a product could be readily obtained from acetone by treatment with a small amount of alkali which would produce a substantial increase in cutting power of a remover as compared with acetone-containing removers otherwise of a similar character.

In an effort to secure the quickest possible action for a paint and varnish remover, I proceeded first with the investigation of the cutting power of various single solvents of different natures, turning then to a mixture of two solvents, three solvents, etc. In this investigation many interesting features have been observed which are illustrated in the table below, the tests being conducted on painted strips as described above:

Table I

Single solvents	Cutting power—seconds
Benzol	3,600
Chlorobenzol	400
Anhydrous methyl alcohol	240
Anhydrous ethyl alcohol	1,020
Isopropyl alcohol (98%)	2,400
Diacetone alcohol	408
Acetone	80
Lugosol (The meaning of this will be explained in a later paragraph)	45
Methyl ethyl ketone	75
Mesityl oxide	210
Furfural	300
Ethyl acetate	105
Binary mixtures	
(In equal parts)	
Benzol-anhydrous methyl alcohol	45
Benzol-anhydrous ethyl alcohol	150
Benzol-acetone	65
Benzol-lugosol	40
Benzol-methyl ethyl ketone	55
Benzol-furfural	90
Benzol-ethyl acetate	75
Acetone-anhydrous methyl alcohol	45
Acetone-diacetone alcohol	115
Acetone-furfural	40
Acetone-mesityl oxide	85
Acetone-methyl acetate	90
Acetone-methyl ethyl ketone	45
Lugosol-anhydrous methyl alcohol	35
Methyl ethyl ketone-anhydrous methyl alcohol	55
Furfural-methyl alcohol	35
Methyl acetate-methyl alcohol	25
Lugosol-mesityl oxide	25
Lugosol-methyl acetate	45
Ternary mixtures	
(In equal parts)	
Benzol-anhydrous methyl alcohol-acetone	50
Benzol-anhydrous methyl alcohol-lugosol	35
Benzol-anhydrous methyl alcohol-methyl ethyl ketone	32
Benzol-acetone-ethyl alcohol	90
Benzol-lugosol-methyl acetate	15
Petroleum naphtha (x)-ethyl alcohol-acetone	155
Petroleum naphtha (x)-ethyl alcohol-lugosol	125

(x) Fraction boiling between 60° C. and 80° C., obtained from commercial petroleum naphtha.

As stated at the beginning of this specification the main feature of the present invention is the use of a product which is obtained from acetone. This product represents a mixture of various ketone condensation products and should be regarded as ketone-condensation-solvent.

Acetone when subjected to the action of certain of the alkali metal hydroxides will undergo intermolecular condensation to form a number of products of higher molecular weight among which mesityl oxide, diacetone alcohol, phoron and iso-phoron are known.

I shall now describe in a general way the preparation of the product which is the subject of the present specification.

To prepare this product, commercial acetone, preferably in pure form, is treated with an alkaline substance capable of causing condensation, forming a certain proportion of products of higher boiling point. Alkaline condensation agents are, for example, quick lime, calcium hydroxide, barium hydroxide and similar alkali metal hydroxides, and the like, insoluble in the acetone; or sodium or potassium hydroxides. The last two hydroxides are preferably used in minute amounts and preferably in such proportions as will dissolve completely in the acetone. The acetone when exposed to a condensation agent of this character, or mixtures of such condensation agents, is permitted to undergo reaction and condensation, preferably at about room temperature for a period sufficient to bring about a substantial equilibrium between the higher boiling form and the acetone. The acetone mixture is then preferably neutralized and subjected to distillation. This may be carried out at ordinary pressure or in a vacuum. It is desirable to avoid acid reaction during distillation and therefore a condition of neutrality approximating the iso-electric point preferably is secured prior to said neutralization step. Various organic and inorganic acids may be used for the neutralization and the employment of gases containing carbon dioxide to form the carbonate or bicarbonate also are not precluded.

In this connection it should be pointed out that with respect to the use of the above product in the present invention it is desirable to avoid the presence of any inorganic material which would remain in solution because any substances which are present in the solvents used for paint and varnish remover usually tend to decrease the cutting power of the solvent. For this reason when neutralizing the alkali-treated acetone it is advisable to use certain acids which form salts insoluble in acetone and in mixtures of acetone and other solvents used in paint and varnish removers. Tartaric acid was found one of the most satisfactory for the purpose.

The material at this stage contains a series of condensation products of acetone, and a large amount of unaltered acetone. The use of this material (after careful neutralization) as such (i. e. without distilling off the unconverted acetone), forms the subject matter of my copending case Ser. No. 289,328 filed June 29, 1928, and is not claimed in the present application. This material is termed, by me, "activated acetone".

After sufficient time for the reaction has elapsed, the alkali-treated acetone is neutralized with a suitable acid and then is usually subjected to a fractional distillation. According to the intended use of the product distillation may be carried on in two ways,

1. Separating unconverted acetone and collecting the products which boil above 60° C. Such a product will contain a mixture of various condensation products and a small amount of acetone and will have a boiling range from 60° C. up to about 170° C. This product I term crude lugosol. Such product is hereinafter, for convenience, termed "lugosol", whether further purified or not.

2. After removing the unconverted acetone fraction the remaining product is fractionated into various fractions having a narrower boiling range.

In connection with the above described method of preparation of ketone condensation solvents (crude lugosol), it should be pointed out that acetone may occur both as normal or ketonic acetone and also as iso-acetone or enolic acetone. Enolic acetone has a structure corresponding to that of unsaturated alcohol (hydroxy propylene). Normal or ketonic acetone presumably exists in equilibrium with iso or enolic acetone.

Enolization apparently plays an important part in the condensation of acetone to form the higher boiling acetone derivatives. My work has shown that when acetone is treated with a small amount of alkali, such as potassium hydroxide to form a higher boiling derivative thereof, that under most advantageous conditions about 1/8th of its volume of diacetone alcohol will be formed with simultaneous formation of about one-eighth of its volume of product boiling between 60° C. and 150° C. In one treatment of alkali an equilibrium is reached in which more than about one-fourth of acetone will undergo condensation with about three-fourths remaining unreacted. I have found that this unreacted acetone, when recovered from one alkali treatment or distillation and when again subjected to the same alkali treatment, is much less reactive than the fresh previously untreated acetone. This I find to be largely due to a lower enolic content and it therefore appears that enolic acetone and not ketonic acetone is the actual substance which will combine with itself (condensation reaction to form such higher boiling derivatives as diacetone alcohol,

etc.). This is also substantiated by the relative differences in the reactivity of commercial acetone derived from various sources.

I have found that certain substances may be added to acetone-alkali reaction mixtures which act as promoters of enolization, and which in consequence increase the yield of condensation products and bring about their formation in less time than would otherwise occur.

Such are substances containing the COH group, i. e., such materials as tertiary alcohols and aldehydes—particularly formaldehyde, are especially suitable as promoters. By the use of such promoters the yield of crude lugosol can be increased to 44% by weight of acetone taken.

The crude lugosol used in the greatest part of examples given in the present specification was made from a commercial grade of acetone by treatment with small amount (.03%) of potassium hydroxide, neutralizing the product of reaction with tartaric acid and distilling off the unconverted acetone. The crude lugosol so obtained after standing in laboratory for a period of several months had the following boiling range:

Temperature range

	Per cent
60 to 70° C.	14
70 to 80° C.	26
80 to 100° C.	32
125 to 140° C.	8
140 to 170° C.	20

The above figures should be regarded only as an illustration of material which may be used in the present invention and in no way am I restricting myself thereto. In practice the distillation range may vary according to the acetone originally used and other physical conditions of reaction.

Referring to the preceding table (Table I) representing the cutting power of various solvents, it should be noted that crude lugosol as compared with other ketone solvents, such as acetone, methyl ethyl ketone, mesityl oxide, and diacetone alcohol, has the quickest action.

The same observation is true for various mixtures of acetone with other solvents, both hydrocarbons (benzol or petroleum naphtha) and non-benzenoid solvents.

Comparing the cutting action of crude lugosol with the action of other active solvents, it should be noted the lugosol is the most effective.

From the same table it should also be noted that while crude lugosol may contain mesityl oxide and diacetone alcohol, it is apparently not the presence of either one of these two substances which produces the effect of a higher efficiency because a mixture of acetone with diacetone alcohol and acetone with mesityl oxide gave a cutting rate much slower than the rate for crude lugosol itself. Therefore it seems that the activity of crude lugosol should be credited to a special combination of various acetone condensation products formed simultaneously in the course of reaction.

While the preferred form of ketone solvent for use in the present invention is crude lugosol, i. e., a product which is substantially free from unconverted acetone, it is also possible to employ to advantage the raw product without distillation obtained by treating acetone with alkali substances as described above. This product was found not as effective or as active as crude lugosol but still had a greater cutting power than the acetone originally used for the preparation of said raw product. This may be seen from the table below which gives the cutting power in seconds as measured on the same kind of wooden strips and by the same method as previously described:

Table II

Solvent mixtures	Treated acetone samp. 1		Treated acetone samp. 2		Treated acetone samp. 3		Lugosol	Acetone
	Alk.	Neu.	Alk.	Neu.	Alk.	Neu.		
Single solvent	90	60	75	60	70	55	45	80
Corresponding solvent:								
+Benzol	70	45	60	45	55	45	40	65
+Petroleum naphtha	200	125	200	130	200	130	100	280
+Methanol	50	30	50	40	45	35	35	45
Corresponding solvent:								
+Benzol and methyl acetate	30	20	40	30	40	25	15	-----
+Benzol and methanol	60	40	55	40	55	40	35	50
+Petroleum naphtha and methyl acetate	60	35	60	35	55	40	32	-----

KETONIC SOLVENTS TESTED

Composition of solvent mixture used in each test	Raw alkali treated acetone						Lugosol	+° Acetone
	Samp. 1		Samp. 2		Samp. 3			
	Alk.	Neu.	Alk.	Neu.	Alk.	Neu.		
Single ketonic solvents	90	60	75	60	70	55	45	80
Binary mixtures of above ketonic solvents with:								
Benzol	70	45	60	45	55	45	40	65
Petroleum naphtha	200	125	200	130	200	130	100	280
Anhydrous methanol	50	30	50	40	45	35	35	45
Ternary mixtures of above ketonic solvents and two other solvents:								
Benzol-methyl acetate	30	20	40	30	40	25	15	-----
Benzol-anhydrous methanol	60	40	55	40	55	40	35	50
Petroleum naphtha-methyl acetate	60	35	60	35	55	40	32	-----

Samples 1, 2 and 3, mentioned in table above were made from acetone using different catalysts for reaction. One thousand cc. of acetone was used in each case and reaction was catalyzed in Sample 1 with one gram of potassium hydroxide; in Sample 2 with one gram of quick lime (calcium oxide) and

in Sample 3 with one gram of barium hydroxide. It can be seen from the above table that the neutral or acidified product is of especial value, the alkaline product giving in all cases a much slower rate of attack.

Having described the general properties and preparation of ketone condensation solvents, which are the main features of the present invention, I will proceed now to give examples of various paint and varnish removers made with the above materials. It is understood that all formulas given below should be regarded only as examples and that I do not wish to restrict myself to the exact proportions given in these formulas. All these examples will preferably include in the formulas paraffin wax as an agent to retard evaporation of the solvents and in some cases will also include nitrocellulose (scrap celluloid) as an agent to increase the consistency of the paint and varnish remover. It should be noted in this connection that the addition of various solids which are capable of dissolving in one of the solvents used in paint and varnish remover will result in cutting down of the "speed" of a given solvent or of a mixture of this solvent and other ingredients, and therefore the cutting speed or rate of attack of wax-containing compositions would be slower than the cutting speed of a corresponding mixture without a wax, for example: Introduction of 1% nitrocellulose of ½ second viscosity into ketonic solvents produced the following change in cutting speed as measured by the method described at the beginning of this application:

Pure acetone	80 seconds	
Acetone containing 1% of nitrocellulose	130 seconds	76% retardation
Lugosol	45 seconds	
Lugosol + 1% of nitrocellulose	70 seconds	55% retardation

It was also observed that when lugosol was used in solvent mixtures containing dissolved solids, such as wax, or nitrocellulose it produced a substantial decrease in the undesirable retardation of the efficiency of a remover, due to the presence of those solids. Retarding action of paraffin wax and of nitrocellulose (½ second cotton) upon the efficiency of various solvents in their mixtures with benzol was determined in the following way:

Various mixtures of benzol with other solvents containing various amounts of paraffin wax in one case, and various amounts of nitrocellulose in the other case were prepared. Approximately an equal amount of each mixture was placed into a test tube and its efficiency was then tested on painted wooden strips, according to the procedure already described. Time of blistering was noted and retardation of the action was calculated in per cent of the action of corresponding solvent mixture without any dissolved solid (as given in Table I).

Results, plated in the form of curves showed that in the case of paraffin wax (curves 1) lugosol-containing mixture had the smallest degree of undesirable drop in efficiency or rapidity of action. In the case of nitrocellulose (curves 2) lugosol-containing mixture was superior to acetone.

This property of lugosol is of undoubtful value for practical application.

All removers made according to the formulas of the examples below were tested on the same kind of painted surface in order to obtain the comparative figures. For this purpose a part of an old automobile (finished with an oil paint) was secured. Each remover was placed on that surface in approximately the same quantity and the time was noted by means of a stop watch when the blistering or wrinkling of the surface was plainly observable. The cutting power will be expressed in the number of seconds which elapsed before the appearance of such wrinkling. Proportion of ingredients is given by volumes including wax, amount of which corresponds to a wax in melted state.

Example 1

Benzol	40 parts by vol.
Anhydrous methyl alcohol	30 parts by vol.
Crude lugosol	30 parts by vol.
Paraffin wax	2 parts by vol.
Cutting rate	145 seconds.

This remover has a satisfactory consistency and a satisfactory slow rate of evaporation. On standing in open air at room temperature for twenty-four hours the loss in weight was slightly over 3%.

Example 2

Petroleum naphtha	30 parts by vol.
Isopropyl alcohol	30 parts by vol.
Crude lugosol	40 parts by vol.
Paraffin wax	2 parts by vol.
Cutting rate	480 seconds.

For corresponding paint and varnish removers containing other ketone solvents the rate of cutting was in all cases slower than for the above remover containing crude lugosol, i. e.:

Acetone	30 parts by vol.
Petroleum naphtha	40 parts by vol.
Isopropyl alcohol	30 parts by vol.
Paraffin wax	2 parts by vol.
Cutting rate	547 seconds.

Petroleum naphtha	30 parts by vol.
Isopropyl alcohol	30 parts by vol.
Methyl ethyl ketone	40 parts by vol.
Paraffin wax	2 parts by vol.
Cutting rate	720 seconds.

Petroleum naphtha	30 parts by vol.
Isopropyl alcohol	30 parts by vol.
Mesityl oxide	40 parts by vol.
Paraffin wax	2 parts by vol.
Cutting rate	1500 seconds.

Example 3

Benzol	40 parts by vol.
Crude lugosol	30 parts by vol.
Methyl acetate	30 parts by vol.
Paraffin wax	2 parts by vol.
Cutting rate	125 seconds.

Example 4

Benzol	45 parts by vol.
Anhydrous methyl alcohol	30 parts by vol.
Crude lugosol	15 parts by vol.
Celluloid scrap	3 parts by weight.
Paraffin wax	7 parts by vol.
Cutting rate	105 seconds.

For corresponding acetone containing remover, i. e:

Benzol	45 parts by vol.
Anhydrous methyl alcohol	30 parts by vol.
Acetone	15 parts by vol.
Celluloid scrap	3 parts by weight.
Wax	7 parts by vol.
Cutting rate	165 seconds.

Example 5

Benzol	40 parts by vol.
Anhydrous methyl alcohol	25 parts by vol.
Crude lugosol	15 parts by vol.
Methyl acetate	15 parts by vol.
Paraffin wax	3 parts by vol.
Cutting rate, from	80 to 90 seconds.

For corresponding acetone containing remover, i. e.:

Benzol	40 parts by vol.
Anhydrous methyl alcohol	25 parts by vol.
Acetone	15 parts by vol.
Methyl acetate	15 parts by vol.
Wax	3 parts by vol.
Cutting rate, about	100–110 seconds.

Example 6

Trichlorethylene	40 parts by vol.
Lugosol	30 parts by vol.
Methyl acetate	20 parts by vol.
Wax	2 parts by vol.
Cutting speed	115 seconds.
Loss in weight in 24 hours	2. 2 per cent.

For corresponding acetone remover, i. e.:

Trichlorethylene	40 parts by vol.
Acetone	30 parts by vol.
Methyl acetate	20 parts by vol.
Paraffin wax	2 parts by vol.
Cutting speed	120 seconds.
Loss in weight in 24 hours	64 per cent.

Example 7

Monochlorbenzol	50 parts by vol.
Anhydrous methanol	25 parts by vol.
Lugosol	25 parts by vol.
Paraffin wax	3 parts by vol.
Cutting speed	120 seconds.
Loss in weight in 24 hours	2. 9 per cent.

For corresponding acetone remover, i. e.:

Monochlorbenzol	50 parts by vol.
Anhydrous methanol	25 parts by vol.
Acetone	25 parts by vol.
Paraffin wax	3 parts by vol.
Cutting speed	125 seconds.
Loss in weight in 24 hours	51. 0 per cent.

Examples 6 and 7 illustrate another advantage of lugosol against acetone which may be very pronounced in some cases, similar to compositions of these examples. This advantage consists in reducing the rate of evaporation of paint and varnish removers, i. e., in reducing the speed of evaporation, which in consequence results in the reduction of an amount of a remover necessary to clean a given area of a painted surface. The ability of a remover to remain wet for a long time in practice is always considered as an advantage. I have observed that rate of evaporation of paint and varnish removers depends largely not only upon relative amount of material capable to arrest evaporation, such as waxes, but also in a large degree upon boiling point and vapor pressure of wax solvents included in a remover. With all other ingredients the same,—higher is the boiling point of such a solvent, and greater will be the rate of evaporation of such a remover, therefore the presence among wax precipitants (non-solvents) of a substance, such as lugosol, which will correct this drawback of high boiling wax solvents, could be considered as a decided advantage.

Curves 3 represents graphically rate of evaporation of four paint and varnish removers mentioned in Examples 6 and 7 and illustrated in above statement.

The rate of evaporation was determined by placing approximately equal amount (20 grams) of each remover into a round tin dish of about 3″ in diameter and about 3/8ths of an inch high. All dishes were then placed in a special thermostat, heated to a desired temperature, and loss in weight was determined at regular intervals.

In reviewing the present application it could be stated that the use of lugosol in paint and varnish removers could be considered as a useful improvement in the art, because it not only introduces a new material into the paint and varnish remover field but this material will enable those skillful in the art to improve their products.

I claim:—

1. A paint and varnish remover compris-

a mixture of liquid alkali condensation products of acetone boiling above the boiling point of acetone.

2. A paint and varnish remover comprising a mixture of liquid alkali condensation products of acetone having a boiling range between 60 and 170° C.

3. A finish remover containing an alkali-polymerized acetone containing a series of products of which the boiling points range from slightly above that of acetone up to 170° C., together with at least one substance selected from the herein described group consisting of benzol, chlorbenzol, methyl alcohol, ethyl alcohol, isopropyl alcohol, diacetone alcohol, acetone, methyl ethyl ketone, mesityl alcohol, furfural, ethyl acetate, methyl acetate and petroleum naphtha.

4. A finish remover containing an alkali-polymerized acetone containing a series of products of which the boiling points range from slightly above that of acetone up to 170° C., together with at least one substance selected from the herein described group consisting of benzol, chlorbenzol, methyl alcohol, ethyl alcohol, isopropyl alcohol, diacetone alcohol, acetone, methyl ethyl ketone, mesityl alcohol, furfural, ethyl acetate, methyl acetate and petroleum naphtha, and a waxy material acting to form an evaporation retarding film on the surface.

5. A finish remover comprising alkali condensation products of acetone and other finish loosening and finish dissolving agents.

6. A finish remover, the rate of evaporation of which is lowered by the presence of liquid alkali condensation products of acetone less volatile than acetone.

7. A paint and varnish remover comprising wax, a wax solvent, methyl acetate and products of alkaline condensation of acetone boiling between about 60 and about 170° C.

8. A paint and varnish remover comprising wax, a wax solvent, "Lugosol" and a co-operating loosening solvent which is a wax precipitant, such remover having a low rate of evaporation.

9. A composite finish remover comprising as a constituent thereof, mixed condensation products of acetone which condensation products can be fractionated by themselves, to yield fractions about as follows:—

	Per cent
60 to 70° C	14
70 to 80° C	26
80 to 100° C	32
125 to 140° C	8
140 to 170° C	20

10. A finish remover as set forth in claim 9, which also contains a wax and a wax solvent.

In testimony whereof I affix my signature.

BORIS N. LOUGOVOY.