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CHANGES OF ZERO IN SPIRIT THERMOMETERS

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CHANGES OF ZERO IN SPIRIT THERMOMETERS

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Abstract.—In an attempt to explain the fall of reading noted over a period of some years in the case of certain spirit thermometers, experiments have been carried out to ascertain the effect of the presence of acetone, in the filling liquid, upon the readings of spirit thermometers over a period of time. It is found that in the case of spirit thermometers containing acetone a marked fall of reading is obtained in course of time when the thermometers are exposed to light. It is suggested that the effect is due to the contraction of the liquid consequent upon the formation of condensation products from the acetone under the influence of light. Acetone is known to be a common impurity in commercial methylated spirit and it is shown that the use of this material either in the commercial or redistilled form should be avoided in the construction of spirit thermometers. No objection appears to attach to the use of pure ethyl alcohol, or acetone-free methyl alcohol, but a mixture of these two substances should be avoided.

In the course of annual inspections at stations, or otherwise, a number of instances have come to light in which the readings of minimum or grass minimum thermometers (in which alcohol is the thermometric substance) have shown a marked fall after some years of use. On examination at the National Physical Laboratory serious changes have, in many cases, been found and it became necessary to institute an investigation into the cause. The results obtained after six months' observations have already been published*. More extended data have now become available, however, and although the main conclusions are confirmed, some modifications are necessary and it has appeared desirable to present the results in a form readily accessible to meteorologists.

Changes in the glass are of importance in the case of mercury thermometers, but are relatively unimportant in the case of spirit thermometers, owing to the large coefficient of expansion of spirit compared with that of glass. In any case the change in volume of the bulb is normally a contraction and not an expansion such as would be required to account for a fall of reading.

Another possible, though improbable, explanation of the fall which received attention was the presence of very minute cracks which might lead to a gradual loss of the spirit. Careful examination failed to reveal any such cracks, and the point was further investigated by enclosing the thermometers in an evacuated space and ascertaining whether the rate of change of the zero was affected. The result of this test was negative so

* *Journal Scientific Instruments*, Vol. III. No. 11 Aug., 1926.

that it would appear that the progressive fall of reading with time was the result of a continued contraction in the volume of the spirit and not a loss by leakage.

There is no evidence that pure ethyl or methyl alcohol would show any change in volume in course of time, but it has been suggested that acetone might be present as an impurity and might prove the cause of the trouble, as acetone is known to form condensation products on exposure to light. Further, acetone is a frequent impurity in methyl alcohol so that it was considered desirable to investigate the behaviour of thermometers in which this material was present intentionally. Experimental thermometers were accordingly constructed and the nature of the materials used in these instruments is shown in Table I.

The thermometers were approximately 16 inches long overall and divided in $\frac{1}{2}°$ Fahrenheit over the range $-20°$ to $+ 110°$ F., the openness of the scale being from $10°$ to $12°$ per inch. The instruments were exposed in a wooden frame on the roof of one of the buildings of the National Physical Laboratory, the tubes being kept vertical to avoid difficulties of drainage of the spirit.

TABLE I.

Thermometer Number.	Liquid Used.	Residual gas above column.
1	Pure ethyl alcohol	Air.
2	,, ,, ,, ...	Nitrogen.
3	Pure methyl alcohol	Air.
4	,, ,, ,, ...	Nitrogen.
5	50% methyl alcohol, 50% acetone ..	Air.
6	,, ,, ,, ,, ,, ..	Nitrogen.

Readings of the ice point were taken every two or three days. In accordance with ordinary experience, thermometers 1 to 4 showed no change in course of time, but it was almost immediately evident that thermometers 5 and 6, which were filled with the acetone-alcohol mixture, showed a relatively large and continued fall in reading. The progressive changes in No. 6 are shown in Fig. 1, in which observations over a period of some thirty-nine months are recorded. Thermometer No. 5. was unfortunately broken in a gale after an exposure of 770 days. During this period the ice reading had fallen to $-65°$F. The nature of these changes will be discussed further at a later stage.

As soon, however, as it was evident that the presence of acetone was playing an important part, the construction of other

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instruments was put in hand, and Table II shows the materials used in the construction of the additional instruments.

TABLE II.

Thermometer Number.	Liquid Used.	Residual gas above column.
7	50% ethyl alcohol, 50% methyl alcohol	Air.
8	Commercial methylated spirit	,,
9	Redistilled methylated spirit	,,
10	Ethyl alcohol, coloured	,,
11	99% ethyl alcohol, 1% acetone ..	,,
12	50% ,, ,, 50% ,, ..	,,
13	,, ,, ,, ,, ,, ..	,,
14	,, ,, ,, ,, ,, ..	Nitrogen.
15	,, ,, ,, ,, ,, ..	,,
16	99% methyl alcohol, 1% acetone ..	Air.
17	98% ,, ,, 2% ,, ..	,,
18	90% ,, ,, 10% ,, ..	,,

The materials employed in the filling of these thermometers and also those previously referred to were specially purified at the Government Laboratory, except in the case of instruments Nos. 8 and 9 in which commercial samples were used. A note by the Government Chemist on the purification of the alcohols is given in the Appendix. The colouring matter employed in No. 10 was the dye used commercially for imparting the familiar red colour to spirit in thermometers when the column is required to be readily visible. The maker was, in fact, instructed to add his usual dye.

The maker was requested to keep the solutions and the instruments in the dark as far as practicable during manufacturing operations and information was also obtained regarding the date of filling and of pointing the tubes.

As soon as received, these instruments were put under observation as in the case of the earlier experimental thermometers with the exception of instruments Nos. 13 and 15 which were carefully protected from light.

The instruments have now been under observation for a period of about 3 years and sufficient information is available regarding the behaviour of the thermometers to enable certain conclusions to be drawn.

In the following paragraphs, the general behaviour of each of the thermometers is dealt with.

Thermometer No. 7.—No appreciable change was found during the first 6 months, but at the end of 1,060 days, the ice reading had fallen from 31·9 to 31·6°F. The difference is too large to attribute to experimental error so that it may be concluded that the use of a mixture of ethyl and methyl alcohol is inadvisable.

Thermometer No. 10.—The use of a red aniline colouring matter has not affected the reading of this instrument. It is of

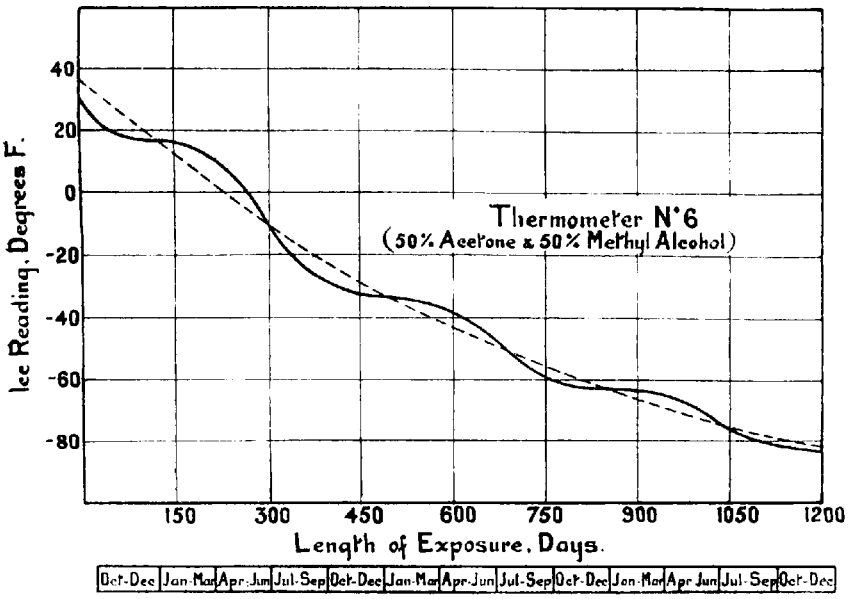
Ice Reading, Degrees F.
40
20
0
-20
-40
-60
-80
Thermometer N°6
(50% Acetone & 50% Methyl Alcohol)
150
300
450
600
750
900
1050
1200
Length of Exposure, Days.
Oct-Dec
Jan-Mar
Apr-Jun
Jul-Sep
Oct-Dec
Jan-Mar
Apr-Jun
Jul-Sep
Oct-Dec
Jan-Mar
Apr-Jun
Jul-Sep
Oct-Dec

FIG. 1.

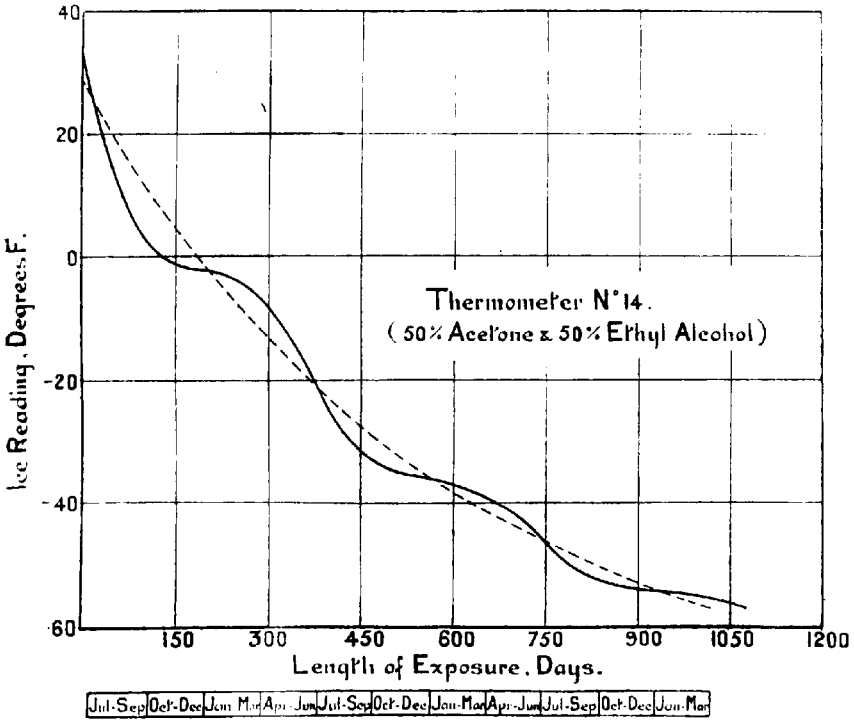
Ice Reading, Degrees F.
40
20
0
-20
-40
-60
Thermometer N°14.
(50% Acetone & 50% Ethyl Alcohol)
150
300
450
600
750
900
1050
1200
Length of Exposure, Days.
Jul-Sep
Oct-Dec
Jan-Mar
Apr-Jun
Jul-Sep
Oct-Dec
Jan-Mar
Apr-Jun
Jul-Sep
Oct-Dec
Jan-Mar

FIG. 2.

interest, however, to record that the colour of the dyed spirit has almost completely faded in the capillary portion of the thermometer although it does not appear to have changed markedly in the bulb. This occurred as the result of six months' exposure only, so that this particular red aniline dye is ineffective after a few months as a means of rendering the column more easily readable in a thermometer freely exposed to daylight.

Thermometers Nos. 12 to 15.—These four thermometers, containing a mixture of equal parts of ethyl alcohol and acetone, were constructed with a view to investigating whether the change of reading of a thermometer in which acetone was present was in any way dependent upon exposure to light and, in consequence, thermometers Nos. 13 and 15 were kept in complete darkness, except for such time as was requisite for taking readings of the ice point, while instruments 12 and 14 were exposed in the usual way. The latter instruments showed changes comparable with the results for thermometers Nos. 5 and 6, but Nos. 13 and 15 remained unaffected over the period during which the observations have extended. Exposure to light, therefore, plays an important part in the effect noted and the result strongly supports the theory already advanced that the change of reading is due to polymerization of the acetone present under the influence of light. In this connexion it is of interest to refer again to thermometer No. 6, the results for which are shown graphically in Fig. 1. The curve there shown exhibits marked periodic fluctuations superimposed on the steady fall of zero. It will be seen that rapid falls occur during the summer months while the curve becomes horizontal during the winter months. Essentially similar effects were shown by No. 14, (Fig. 2) and by No. 12.

Since it has been shown that the fall of zero is conditioned by exposure to light, this seasonal fluctuation is readily explained by the variation in the duration and intensity of daylight during the year. The curves for both thermometers show a tendency for the rate of fall of zero to decrease with the time of exposure. In Figs. 1 and 2 the full lines represent the actual observations, while the dotted lines show the general trend of the curves apart from seasonal variations. It will be noted that these dotted curves pass approximately through the points where the rate of change of the observations have maximum and minimum values. It may also be remarked that the tests with thermometers Nos. 12 to 15 do not indicate any marked difference between thermometers containing air or nitrogen as residual gas.

Thermometers Nos. 16 to 18.—The tests previously discussed have referred to thermometers in which acetone has been present in a large proportion, namely, 50 per cent. of the filling liquid. This is a much larger proportion than is likely to occur in practice if the acetone is merely present as an impurity in the spirit used, consequently, in order to investigate the effect of smaller quantities a series of three thermometers was made up containing 1, 2 and 10 per cent. of acetone, the remaining material in each case being

methyl alcohol. These instruments again show a similar fall of reading in course of time and, in general, the fall is smaller for the smaller percentage of acetone present. The results are shown in Fig. 3.

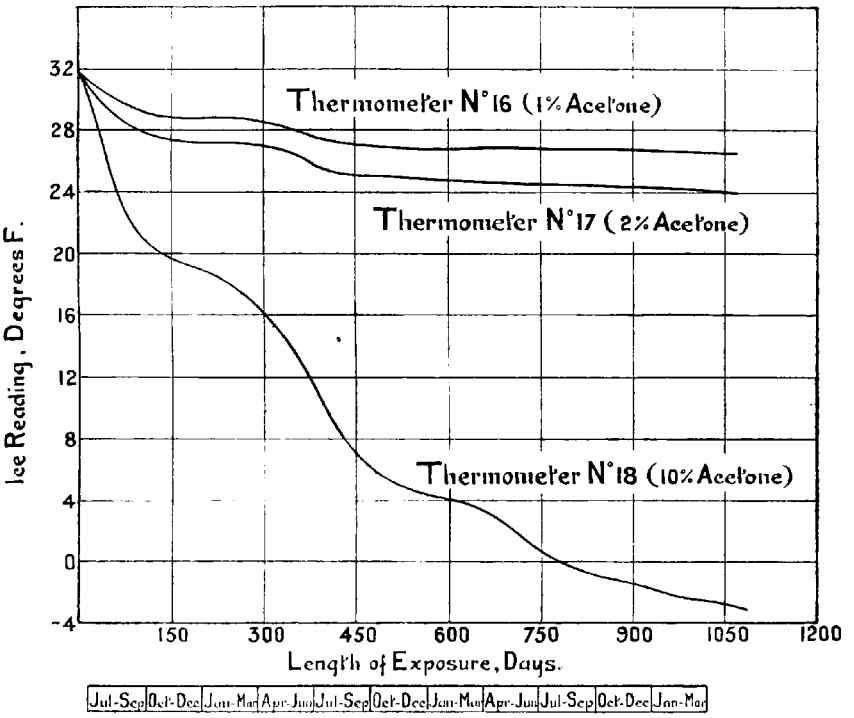

FIG. 3.

It will be seen that of the addition of only 1 per cent. of acetone produces a fall of zero amounting to 4°F. in one year and to nearly 5°F. in three years. Doubling the percentage of acetone does not double the rate of change of zero, the effect of adding a given amount of acetone being relatively smaller as the percentage of acetone is increased. The curve for No. 18 (10 per cent. acetone) shows clearly the seasonal effect previously discussed and all three curves also show the gradual falling off with time in the effect of the acetone. This is particularly noticeable in the curve for No. 16 (1 per cent. of acetone). In this thermometer there was very little change after 500 days.

Thermometer No. 11.—This instrument shows a fall of ice reading from 32·0°F. to 27·0°F. over a period of 1060 days; the amount of fall agrees fairly closely with that of thermometer No. 16 which also contains 1 per cent of acetone, the difference between the two thermometers being that the remaining liquid is ethyl alcohol in the one case and methyl in the other.

Thermometers Nos. 8 and 9.—The two remaining thermometers were filled respectively with commercial methylated spirit and redistilled methylated spirit to ascertain whether these materials could be employed satisfactorily in the place of the more expensive pure alcohol. The results are shown in Fig. 4. and indicate that neither of the samples could be used for spirit thermometers. It may be inferred that about $\frac{1}{2}$ per cent. of acetone was present in each case. The seasonal effect is well marked during the earlier halves of both curves and the steadying effect of prolonged exposure may also be observed, though not to so marked an extent as in No. 16. It should perhaps be remarked that the curves in Fig. 4 are not necessarily typical of methylated spirit as a thermometric substance. In a thermometer filled with spirit from a bottle which had been exposed freely to light for many years it is possible that no perceptible change of zero would occur. It is clear, however, that the use of such a material, either crude or redistilled, involves great risk of large changes of zero within so short a period as 12 months and should, therefore, be avoided.

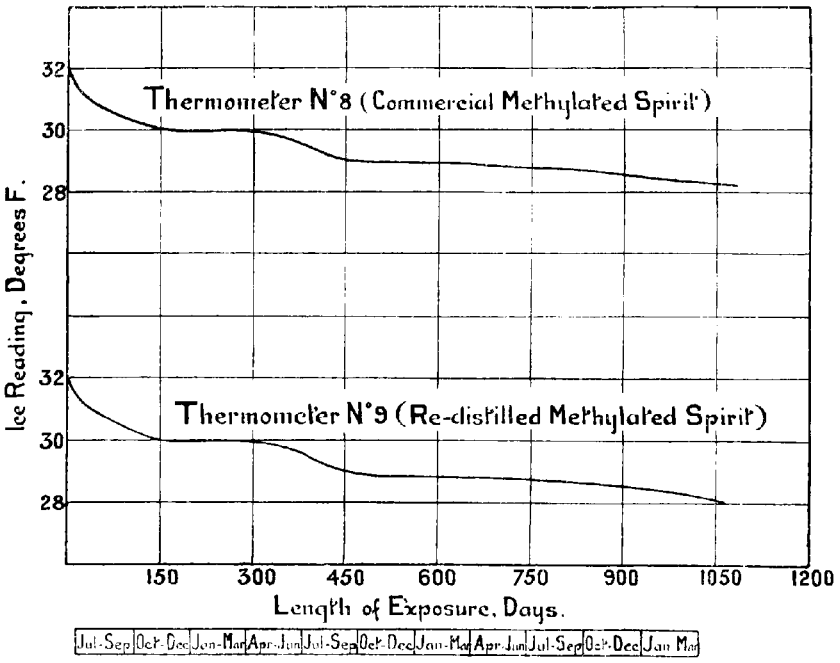

FIG. 4.

CONCLUSIONS.

(1) In selecting a liquid for filling spirit thermometers, the presence of acetone as an impurity in the spirit should be carefully guarded against. A guarantee of freedom from acetone should be demanded from the firm supplying the spirit.

(2) Owing to the common presence of acetone as an impurity in methylated spirit obtained from the usual sources, the use of this material, either in its commercial form or when redistilled, should be avoided.

(3) Thermometers filled with either pure methyl or ethyl alcohol are stable over long periods.

(4) The use of a mixture of ethyl and methyl alcohol should be avoided.

(5) The addition of aniline colouring matter to pure ethyl alcohol does not affect the stability of the zero.

(6) The nature of the residual gas, whether air or nitrogen, does not appear to affect the subsequent behaviour of the instrument.

(7) The depression of zero associated with the presence of acetone occurs only on exposure to light.

Thanks are due to the Government Chemist who supplied specially purified samples of ethyl alcohol, methyl alcohol and acetone for use in this investigation, and to the Director of the National Physical Laboratory for providing the facilities for carrying out the tests.

APPENDIX.

Note by the Government Chemist on the Purification of Alcohols.

The alcohols were obtained from Messrs. Hopkin & Williams, 16 Cross Street, Hatton Garden, E.C. and were described by them as "Methyl Alcohol, Puriss., Free from Acetone" and "Absolute Alcohol, Ethyl", respectively. They were found, on examination, to be very good specimens which might have been sufficiently pure for the purpose as they stood but as will be seen from the results of analysis given below, they were still further purified by the following treatment in this Laboratory :—

The alcohols were just acidified with a few drops of concentrated sulphuric acid and distilled. The distillates were made just alkaline with a small piece of caustic potash and again distilled. The distillates were then fractionally distilled through a Young's 5-evaporator still head at the rate of one drop per second and collected in three fractions ($\frac{1}{5}$; $\frac{3}{5}$; $\frac{1}{5}$). The first and third fractions were rejected.

METHYL ALCOHOL.

	As purchased.	After treatment in Laboratory.
Density 15°·56C/15°·56 ..	798·8 = 99·5% methyl alcohol.	796·4 = 100% methyl alcohol.
Acetone, grams per 100 c.c. ..	<0·04	<0·04
Acid	nil	nil
Esters	nil	nil
Formaldehyde	nil	nil
Amine reaction	12 c.c. + 12 c.c. water + one drop of p. nitrophenol solution required 3 drops $\frac{n}{10}H_2SO_4$ to discharge colour	Nil—Colour discharged on adding one drop $\frac{n}{10}H_2SO_4$

ETHYL ALCOHOL.

	As purchased.	After treatment in Laboratory.
Density 15°·56C/15°·56C ..	796·1 = 99·5% ethyl alcohol	796·0 = 99·5% ethyl alcohol.
Acid, parts per 100,000 ..	8·4	nil
Esters	nil	nil
Forfural	nil	nil
Aldehyde, parts per 100,000 ..	12·0	4·0
Higher Alcohols	nil	nil
Amine reaction	10 c.c. + 10 c.c. water + one drop p. nitrophenol solution gave a yellow colour on adding one drop of $\frac{n}{10}$Na OH.	nil (Colour discharged on adding one drop of $\frac{n}{10}H_2SO_4$)

The acetone was prepared from commercial rectified acetone by treatment with anhydrous sodium iodide according to the process described in the *Journal of the Chemical Society* 1913, p.1255. It has a boiling point of 56°·05 — 56°·10C. and is free from amines.

(sgd.) R. ROBERTSON.