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FIRED ELECTRICAL RESISTOR COMPRISING MOLYBDENUM DISILICIDE AND BOROSILICATE GLASS FRIT

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This invention relates to electrical resistors. More particularly, it relates to the preparation of composition type resistors having many properties which were hitherto considered unattainable except in wire wound resistors.

Resistors are usually selected for various applications on the basis of properties and cost. The major types of resistors in present use are either composition or wire wound. Many composition resistors are known, based on carbon compacted with a suitable binder. They are low in first cost and are widely used where the low power dissipation, high noise level and poor stability inherent in such compositions may be tolerated. Although wire wound resistors are more expensive, they are used where stability, better power dissipation and greater accuracy in resistance values are desired. In addition to a higher first cost, the major disadvantage of wire wound resistors is their high reactance at high frequencies, which is in contrast with the tendency of composition resistors to act as pure resistance at high frequencies. Wire wound resistors are made by wrapping lengths of special resistance wire around an insulating core or form. For a specific resistance value, wire wound resistors are generally larger than composition resistors, and where space is at a premium, this may serve to limit the applicability of wire wound resistors.

This invention is directed to resistor elements in which the better properties of both composition and wire wound resistors are obtained. Essentially our novel resistors are of the composition type, and while retaining the valuable characteristics of this type, our resistors have been found to also possess excellent stability and high power dissipation. Composition resistors are not generally produced with ratings of more than about 2 watts. When, however, the compositions prepared in accordance with our findings are formed into resistors, it is possible to produce stable products having ratings from as low as 0.1 ohm to 10^{12} ohms. Resistors produced in accordance with this specification have been operated at 10 watt loads at 1000° F. ambient temperatures and at 40 watt loads at somewhat lower temperatures without appreciable change in resistance. In addition, by suitably proportioning the constituents in our composition and by properly adjusting the firing conditions, resistors can be made with voltage coefficients which are either negative or positive and with temperature coefficients which will be within the specifications normally set for both composition and wire wound resistors. It is especially significant that resistors may be produced in which the temperature coefficients of resistance are substantially zero.

The essential constituents of our novel composition resistors are molybdenum disilicide and certain powdered glasses. We have found that when these constitutents are combined in specified proportions and fired in the range of about 1400° to about 1700° F. under a suitable atmosphere, resistors with the desired properties are produced having resistivity values from as low as 0.05 ohm cm. to 100,000 ohm cm. or more. We have further found that the addition to the glass composition of molybdenum

oxide enables us to produce resistors with even further enhanced properties. We have further found that the addition of alumina to the mixture enables us to more readily produce resistors with temperature and voltage coefficients which essentially are zero for a wider range of compositions.

The molybdenum disilicide may be obtained commercially of a purity sufficient for our purposes. We may, however, manufacture our molybdenum disilicide from molybdenum metal and silicon by sintering together powders of these materials, crushing and resintering and recrushing one or more times until a completely homogeneous product results.

The glasses used in our invention are required to have the following general characteristics:

(1) The constituent oxides of the basis glass should not include any compounds, except MoO_3, which would be reduced by $MoSi_2$ during the process of manufacture of the resistors.

(2) The glass should remain vitreous during the sintering step and should not devitrify when powdered and sintered during the firing of the resistors.

(3) The glass should be capable of being smelted at practical temperatures and should have a high degree of durability, i.e., it should be substantially insoluble in water, mild acids or other anticipated environments.

(4) The glass should possess a coefficient of thermal expansion not appreciably different from that of the fired resistor and preferably of the order of 15% less than that of the remainder of the composition.

A typical composition representative of the glasses which may be used is as follows:

RO (Mols) 1 Mol	R_2O_3 (Mols) .653 Mols	RO_2 (Mols) 3.56 Mols
.260 BaO .300 CaO .166 MgO .274 $(K, Na)_2O$	.600 B_2O_3 .053 Al_2O_3	3.56 SiO_2

Such a composition may be prepared from readily available raw materials blended in the following proportions:

Raw material:	Percent by weight
Borax, anhyd.	14.6
Colemanite	1.9
Clay, kaolin	4.6
$CaCO_3$	7.0
$MgCO_3$	3.7
$BaCO_3$	13.7
SiO_2	54.5
	100.0

The above composition was found to possess all of the desired properties and is merely representative of one which is suitable for the purpose. Many other glass compositions can be used.

The preparation of this glass is accomplished by melting the charge by heating to 2600° F.; quenching, preferably in water, and finally grinding the frit to minus 200 mesh (Tyler Standard), for example, in a porcelain ball mill. The dried frit is then ready for use.

In addition to molybdenum disilicide and glass frit, our novel composition resistors may contain a material which when heated with the remaining constituents may be reduced. One such material, preferred by us, is molybdenum trioxide. Other materials, such as molybdates which furnish molybdenum trioxide under the process conditions, may be employed. While we do not wish to be bound by any particular hypothesis, we believe that the molybdenum oxide promotes the formation of a good

bond between the molybdenum disilicide and the glass during the firing of the resistors. It is believed necessary to saturate the bonding layer of the glass with an oxide of molybdenum. One method of accomplishing this would be to heat the molybdenum disilicide-glass mixture for a sufficiently prolonged period of time, to permit the bonding layer of the glass to become saturated with an oxide of molybdenum, derived from the molybdenum disilicide. In the presence of high concentrations of the latter, the oxide is believed to be reduced to a suboxide and a bond results between the disilicide and the glass. We have found, in order to achieve a satisfactory bond in a practicable sintering time, that the presence of molybdenum oxide or its equivalent is highly desirable.

Another advantage derived from the inclusion of molybdenum oxide in our composition, is the ready formation of a "conducting glass" upon firing in contact with molybdenum disilicide. Resistors of this type, as will be illustrated later, have been made with $MoSi_2$, making up less than 20% by volume of the compact. It is obvious, therefore, that the molybdenum disilicide could not form a continuous conducting phase in this case. The glass, which would form a continuous matrix through the resistor, must be a primary conducting medium. One reasonable explanation of this phenomenon would seem to be that the molybdenum oxide is reduced during firing and results in the glass becoming an electrically conducting medium. Reduction of the molybdenum trioxide would necessitate oxidation of a portion of the molybdenum disilicide which then may possibly dissolve or diffuse into the glass, thus increasing the current carrying power of the vitreous portion. It has been determined that the quantity of molybdenum oxide in the glass is one of the factors which determine the resistivity in these compositions.

It has been found that a further ingredient may advantageously comprise a portion of our novel composition resistors prepared from molybdenum disilicide and glass frit. This is an insulating refractory oxide, such as alumina or zirconia, which dissolves only slightly or not at all in the glass. While we do not completely understand the function of this constituent, it has been observed that resistor compositions containing substantial amounts of alumina may possess desirably small or zero voltage coefficients or temperature coefficients of resistance in addition to the required resistivity, over a wider range of composition than similar resistors from which the alumina is absent.

The preparation of resistors from the above described constituents follows, in general, standard ceramic techniques. The glass component is prepared by mixing a batch from the raw materials as above described, melting the batch, quenching the melt, preferably in water, to form a frit and grinding the frit to a powder by ball milling or other comminuting procedures. The resulting powder is dried and is then mixed with powdered molybdenum disilicide in the required proportions. If molybdenum oxide is included in the composition, it may be added either to the glass batch before fritting or to the mixture of powdered glass and powdered disilicide. In instances where alumina or zirconia or other refractory oxide is to be added, it should be included in the mixture of already formed glass powder and disilicide. The mixture of glass powder, molybdenum disilicide and any other optional constituents is shaped by conventional techniques, such as pressing or extrusion. In shaping the mixture, organic plasticizers are sometimes useful, but we have found that these must be chosen from among those which can be removed by heating under an inert or reducing atmosphere before the remaining constituents sinter. After the mixture has been shaped, the shapes are dried and the resistors are then fired to produce the finished article. Firing temperatures of between about 1400° F. and 1800° F. have been found suitable for most compositions. Firing is preferably carried out under an inert or reducing atmosphere such as argon, helium, nitrogen, hydrogen or combinations such as forming gas (93% N_2, 7% H_2) or cracked ammonia. Resistors formed without organic additives or from which these additives have been subsequently removed may be fired by introducing the ware directly into the furnace at temperature. This is not a necessary procedure to this invention but simplifies both control and production.

Frits designated A–E with 0, 1, 3, 6 and 9.6% by weight of molybdenum oxide respectively were prepared from suitable raw materials to produce products having the following analyses, reduced to oxides:

TABLE I

Composition of frits—designation and weight percent of oxides

Frit Designation	A	B	C	D	E
MoO_3	None	1.00	3.00	6.00	9.6
SiO_2	62.60	62.00	61.73	58.96	56.60
B_2O_3	12.27	12.14	11.90	11.48	11.07
Al_2O_3	1.57	1.55	1.52	1.47	1.42
BaO	11.72	11.60	11.38	11.00	10.60
MgO	1.96	1.94	1.89	1.83	1.77
CaO	4.60	4.85	4.75	4.60	4.44
Na_2O	4.98	4.92	4.83	4.66	4.50
	100.00	100.00	100.00	100.00	100.00

In the following table there are tabulated electrical data on various compositions in which frits of the above analyses were blended with varying amounts of molybdenum disilicide and alumina. Samples of the following compositions were pressed at about 10,000 p.s.i. and fired to produce specimens having the following dimensions: length 2.00 inches, width 0.370 inch, and thickness 0.112 inch. The samples prepared as above described were introduced into a furnace already at the firing temperature and held at the indicated temperature for 30 minutes. "R" is the resistance of the specimen with clip contacts, reported in ohms. "V.C." is the voltage coefficient in percent per volt from highest to lowest load available. The load varies with the resistance of the sample.

TABLE II

Code	$MoSi_2$ (Percent)	Frit (Percent)	Al_2O_3 (Percent)	Firing Temp. (° F.)	R (ohms)	V.C. (Percent/volt)
831	40	B-55	5	1,425	1,000,000	Not meas.
	40	B-55	5	1,450	13,354	+0.001
	40	B-55	5	1,475	5,200	+0.021
833	40	B-57	3	1,425	26,000	Not meas.
	40	B-57	3	1,450	4,958	+0.020
	40	B-57	3	1,475	5,052	+0.104
834	40	B-59	1	1,425	68,906	Not meas.
	40	B-59	1	1,450	8,096	+0.025
	40	B-59	1	1,475	Not meas.	−0.188
835	42	B-55	3	1,425	18,221	+0.032
	42	B-55	3	1,450	3,490	+0.032
	42	B-55	3	1,475	5,390	+0.241
836	44	B-55	1	1,425	2,329	+0.117
	44	B-55	1	1,450	739	+0.42
	44	B-55	1	1,475	1,165	−0.332
830	45	B-50	5	1,425	4,330	+0.030
	45	B-50	5	1,450	1,310	+0.061
	45	B-50	5	1,485	645	+0.048
829	49	B-46	5	1,425	1,417	+0.001
	49	B-46	5	1,450	360	+0.078
	49	B-46	5	1,485	217	+0.032
828	52	B-43	5	1,450	3,228	−0.282
	52	B-43	5	1,465	988	−0.499
	52	B-43	5	1,475	90	+0.424
827	54	B-41	5	1,425	591	+0.006
	54	B-41	5	1,430	1,230	−0.0228
	54	B-41	5	1,450	529	−0.008
826	56	B-39	5	1,425	309	+0.049
	56	B-39	5	1,450	543	−0.234
825	58	B-37	5	1,425	708,700	−0.869
	58	B-37	5	1,440	4,913	−0.260
	58	B-37	5	1,450	108	+0.234
	58	B-37	5	1,475	48	+1.08
824	60	B-35	5	1,425	707,310	+0.772
	60	B-35	5	1,440	2,595	−0.288
	60	B-35	5	1,450	95	+0.394
	60	B-35	5	1,475	40	+2.04

TABLE II—Continued

Code	$MoSi_2$ (Percent)	Frit (Percent)	Al_2O_3 (Percent)	Firing Temp. (° F.)	R (ohms)	V.C. (Percent/volt)
809	56	C-35	9	1,625	514	+0.254
	56	C-35	9	1,675	328	+0.339
811	56	B-35	9	1,625	913	+0.181
	56	B-35	9	1,675	682	+0.305
821	56	C-31	13	1,575	2,212	+0.026
403	55	D-45	0	1,500	308	−0.84
404	55	D-45	0	1,475	72.8	+0.06
400	57	D-43	0	1,800	93.8	+0.09
	57	D-43	0	1,450	32,600	−0.30
406	59	D-41	0	1,450	1,350	−0.35
407	61	D-39	0	1,450	1,680	−0.15
408	63	D-37	0	1,450	607	−0.29
409	65	D-35	0	1,450	557	−0.54
410	65	D-35	0	1,420	608	−0.22
	65	D-35	0	1,440	70.3	+0.23
401	57	E-43	0	1,500	10,000	−0.48

We have found, as illustrated by the data in Table II, that the resistance of a composition decreased with increased firing temperature. The resistance also decreased with higher molybdenum disilicide content and with lower content of glass frit, but increased with higher alumina content. For a particular composition, the voltage coefficient became increasingly positive with higher firing temperature, i.e., the voltage coefficient at low firing temperatures had a relatively large negative value. With increasing firing temperatures, the voltage coefficient decreased in negative value, passed through zero and then increased in positive value. It is therefore possible with compositions within the scope of our invention, to achieve zero voltage coefficients, or at least to achieve very low voltage coefficients with proper control of firing temperature.

Although the application of the widely different voltage employed in the determination of the voltage coefficient generates considerably different quantities of heat in the resistors. As a result any variation of resistance with temperature is actually measured as a part of the measured voltage coefficient. Much of the apparent variability in the data shown in Table II may possibly be explained by this fact.

Further information was therefore obtained on the temperature coefficient (in percent/° C.) of certain of the resistor compositions developed. For this purpose, the resistance was measured at room temperature and at 155° C. with a Wheatstone bridge operating at 3 volts. Before each measurement the test specimens were allowed to reach temperature equilibrium.

The temperature coefficients "T.C." tabulated are indicative of the change in resistance with change in temperature, e.g., such changes as are incidental to the use of the resistor. The values reported were obtained by measuring the resistance of a specimen at room temperature and at an elevated temperature, between 150° C. and 160° C., and dividing the change in resistance by the original resistance and by the difference in temperature and expressing the result as a percent, per degree centigrade. The results are reported in the following table.

TABLE III

Code	$MoSi_2$ (Percent)	Frit (Percent)	Al_2O_3 (Percent)	Firing Temp. (° F.)	R (ohms)	T. C. (Percent/° C.)
831	40.0	B-55.0	5.0	1,520	4,900,000	−0.093
				1,525	64,060	−0.073
				1,557	8,410	−0.007
				1,563	4,566	+0.011
				1,568	4,552	+0.017
				1,595	1,961	+0.020
				1,624	296	+0.030
837	42.1	B-57.9		1,498	156,800	−0.145
				1,540	6,904	+0.012
				1,546	1,894	+0.021
838	41.3	B-56.7	2.0	1,498	435,000	−0.069
				1,548	166,100	−0.048
				1,556	48,410	−0.018
				1,566	14,700	−0.011

TABLE III—Continued

Code	$MoSi_2$ (Percent)	Frit (Percent)	Al_2O_3 (Percent)	Firing Temp. (° F.)	R (ohms)	T. C. (Percent/° C.)
844	37.0	B-58	5.0	1,556	3,300,000	−0.175
				1,570	135,700	−0.079
				1,584	122,000	−0.021
				1,602	5,844	−0.001
				1,624	1,593	+0.007
				1,641	575	+0.029
845	43.0	B-52.0	5.0	1,502	12,700	−0.026
				1,523	3,130	+0.022
				1,537	2,620	+0.036
				1,556	1,400	+0.024
				1,602	321	+0.041
849	54.0	C-41.0	5.0	1,401	357	+0.010
				1,476	92	+0.014
				1,500	60	+0.026
				1,542	29	+0.031
				1,561	14	+0.058
850	40.0	C-55.0	5.0	1,398	88	−0.059
				1,450	83	+0.032
				1,500	66	+0.043
				1,525	42	+0.055
				1,561	42	+0.062
851	37.0	C-55.0	8.0	1,500	1,700,000	−1.580
				1,522	132,300	−0.158
				1,574	22,240	−0.038
				1,588	10,004	−0.006
				1,613	1,043	+0.060
852	51.0	C-41.0	8.0	1,433	91,400	−0.212
				1,470	564	−0.027
				1,496	278	+0.030
				1,555	155	+0.040
853	66.6	C-28.6	4.8	1,404	1,910,000	−0.159
				1,433	3,730	−0.142
				1,451	436	−0.033
				1,470	70	+0.136
857	20.0	C-80.0		1,480	547,000	−0.303
				1,542	1,800,000	−1.730
858	35.0	A-60.0	5.0	1,542	165,400	−0.366
859	25.0	A-70.0	5.0	1,542	516,000	−0.341
860	15.0	A-80.0	5.0	1,542	4,400,000	−0.347
841	42.1	D-57.9		1,539	11,850	−0.033
				1,557	28,010	−0.036

From the data tabulated above, it will be seen that the variation of resistance and temperature coefficient follows the same pattern as the variation in resistance and voltage coefficient, except that the trends are somewhat more distinct due to the more uniform conditions of the test. Thus the resistance of a composition tends to decrease as the firing temperature is increased, and the temperature coefficient tends to become increasingly positive with increase in firing temperature, changing from a large negative value at low firing temperatures to lower negative values, thence through zero and thence to increasingly larger positive values, as the firing temperature is raised.

Thus by suitably controlling the relative proportions of molybdenum disilicide and glass frit and alumina and molybdenum oxide, as well as the firing conditions, it becomes possible to produce resistors with voltage coefficients and temperature coefficients which are zero or other low values sufficiently low to meet the desired specification for any intended use.

All of the above compositions enumerated in Tables II and III may be satisfactorily employed as electrical resistors. Thus our invention comprises resistor compositions consisting essentially of molybdenum disilicide and a glass frit, with or without either or both of the additives: alumina or molybdenum oxide or their equivalents. Broadly our preferred compositions may contain between about 15% and 65% by weight of molybdenum disilicide, between about 25% and 85% of glass frit, up to 10% by weight of molybdenum oxide, either as a separately added component or as a constituent of the glass frit or as both, and up to 20% of a refractory oxide such as alumina or zirconia.

In commercial resistors, it is ordinarily desirable to have very low voltage coefficients, for instance, under 0.035%/volt, and since the voltage coefficient may depend on the composition as well as the firing treatment, a preferred composition range would embrace between 30% and 65% by weight of molybdenum disilicide, about 25% to 65% by weight of the glass frit and zero to 15% of alumina. Such compositions should preferably con-

tain up to about 10% of molybdenum trioxide or a substance which supplies the oxide. Such compositions would be formed into shapes with the desired dimensions and fired at temperatures depending somewhat on the particular composition, of between about 1400° F. and 1700° F. As shown by the above data, a still more preferred range of resistor compositions comprises $MoSi_2$ amounting to between about 40 and 55% by weight, between about 41 and 59% by weight of a glass frit containing 1% MoO_3 and between about 1 and 5% by weight of alumina, formed into shapes and fired at temperatures between about 1425° F. and 1484° F., in a suitable atmosphere.

We claim:

1. A resistor consisting of a fired mass made from an unfired composition consisting essentially of between about 15% and 65% by weight of molybdenum disilicide, up to 20% by weight of a refractory oxide from the group consisting of alumina and zirconia, up to 10% by weight of molybdenum oxide and the remainder comprising between 25% and 85% by weight of the composition, a borosilicate glass frit.

2. An electrical resistor consisting of a fired body made from an unfired composition consisting essentially of between about 15% and 65% by weight of molybdenum disilicide and the balance a borosilicate glass.

3. An electrical resistor consisting of a fired body made from an unfired composition consisting essentially of between about 15% and 65% by weight of molybdenum disilicide, between about 1% and 10% by weight of molybdenum oxide and the remainder a borosilicate glass frit.

4. An electrical resistor having a voltage coefficient below about 0.035%/volt consisting of a body formed by firing an unfired composition consisting essentially of: between about 30% and 65% by weight of molybdenum disilicide, up to 15% by weight of alumina, up to 10% by weight of molybdenum oxide and the remainder, comprising between about 25% and 65% by weight of the composition, a borosilicate glass frit.

5. An electrical resistor consisting of a fired body consisting essentially of between 40% and 55% by weight of molybdenum disilicide, between about 41% and 59% by weight of a borosilicate glass containing about 1% molybdenum oxide, and between about 1% and 5% by weight of alumina.

6. A method of producing electrical resistors with predetermined voltage coefficients and temperature coefficients, which comprises: preparing a composition consisting essentially of between about 15% and 65% by weight of molybdenum disilicide, up to 20% by weight of a refractory oxide from the group consisting of alumina and zirconia, up to 10% by weight of molybdenum oxide and the remainder comprising between 25% and 85% by weight of the composition, a borosilicate glass frit, proportioning the constituents to produce the required resistance in a fired body, shaping the composition and firing the shaped composition at the temperature of not less than 1400° F. in an atmosphere selected from the group consisting of reducing and inert atmospheres and for the time required to produce a fired body with the desired coefficients.

7. The method of claim 6 in which the composition before firing consists of between 30% and 65% by weight of molybdenum disilicide and between about 25% and 65% by weight of the glass frit, up to 15% by weight of alumina and up to 10% by weight of molybdenum trioxide.

8. The method of claim 6 in which the composition before firing consists of between about 40% and 55% by weight of molybdenum disilicide, between about 1% and 5% by weight of alumina and between about 41% and 59% by weight of a borosilicate glass frit containing about 1% molybdenum oxide.

9. The method of claim 6 in which the composition before firing contains molybdenum trioxide added as a constituent of the frit.

10. The method of claim 6 in which the composition before firing contains molybdenum trioxide added as a separate component to the batch to be shaped and fired.

11. The method of claim 6 in which the composition before firing contains molybdenum trioxide part of which is a constituent of the glass frit and part of which is added as a separate component of the batch to be shaped and fired.

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