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HARDENABLE ALLOY STEELS RESISTANT TO SOFTENING AT ELEVATED TEMPERATURES

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6 Claims. (Cl. 75—126)

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This invention pertains to alloy steels of the class that are suitable for use in cutting tools and the like, which are hardenable by quenching and which undergo secondary hardening on subsequent tempering, and pertains more particularly to an alloy steel of this type having a balanced composition such as to impart to the steel in the quenched and tempered condition, a high degree of resistance against softening when subjected to elevated temperatures especially within the range extending upward of about 1100° F.

It is the object of this invention to provide a relatively low cost alloy steel of relatively low total alloy content, which, after being heat treated, has better resistance to softening at temperatures upwards of about 1100° F. than steels now available. Steel of such characteristics is useful in power plant equipment in the form of bolts, studs, turbine wheels, blades and buckets; in the forging and die-casting industries for hot work dies, cores, mandrels and punches; and in the machining industry for cutting tools.

The steel of the invention contains, as essential constituents, chromium, vanadium, tungsten and molybdenum within broad limits of about, 0.5 to 3% Cr, 0.2 to 2% V, 1 to 3% W and 0.5 to 4% Mo, together with 0.3 to 1.2% carbon, a more preferred range being about, 1 to 2.5% Cr, 0.5 to 1.5% V, 1 to 3% W and 0.5 to 3% Mo, together with 0.4 to 0.9% carbon. The balance of the composition is substantially iron, except for optional additions of up to about 3% in aggregate of other elements which do not substantially impair the elevated temperature resistance of the quenched and tempered steel, against softening. Thus, for example, manganese may be present up to about 1%, and silicon up to about 2%, the latter for imparting scale resistance in some analyses.

The essential constituents aforesaid are, in accordance with the invention and for reasons explained below, present in a balanced composition such that the sum of $\frac{1}{10}$ the chromium

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content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content, and $\frac{6}{100}$ of the molybdenum content shall total at least 0.3% but shall not exceed 0.15% plus the carbon content. Also for assuring forgeability of the steel, the aforesaid sum should not exceed about 1.0%.

It it well known that steels other than those which are sufficiently high in alloy content to be substantially austenitic at room temperature, lose their strength, i. e., hardness, fairly rapidly as the temperatures to which they are heated exceed about 1000° F. Some steels containing the carbide forming elements chromium, vanadium, tungsten and molybdenum, are much more resistant than other steels to this weakening at elevated temperatures, because when they are properly heat treated there occurs in them a precipitation of alloy carbides at temperatures upwards of about 1000° F., and this precipitation prevents or retards the softening or weakening at high temperatures. The heat treatment referred to involves a heating to a temperature high enough to cause an appreciable amount of carbon to dissolve in the steel; followed by a cooling to approximately room temperature at a sufficiently rapid rate to prevent much precipitation of the carbides during the cooling; and finally, a tempering at about 1000° to 1200° F.

It has been generally accepted that the larger the amount of carbide forming elements in the steel, the greater is the resistance of the steel to softening at temperatures upwards of about 1000° F. This has been well illustrated by E. C. Bain in Chapter VI of his book "Functions of the Alloying Elements in Steel." Now I have discovered, and this is the basis of my invention, that the resistance to softening particularly at temperatures upwards of about 1200 F. may decrease in some steels as the amount of the alloying elements increases. This is illustrated in the following Tables I to III inclusive. To get the data for these tables, the samples treated were first heated to 2350° F. to assure thorough solution of carbides and then were quenched. They were tested for hardness after cumulative reheatings

at the successively higher temperatures indicated in the tables.

TABLE I

Effect of chromium on hardness of steels after tempering

Bar	Analysis, Per Cent					Rockwell C Hardness, After Cumulative 2 Hour Temperings At—				
	C	Cr	V	W	Mo	1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
5805	.41	1.25	.56	.95	.75	48.5	47.5	44.5	41	33.5
5806	.37	1.97	.55	.93	.72	48.5	46	42.5	38.5	32.5
5807	.40	3.09	.54	.93	.71	49.5	46	41	35.5	29.5
5753	.41	2.26	.59	.65	.46	48.5	46	41	36.5	30
5759	.41	3.30	.60	.65	.45	48.5	44	37	32.5	28
5809	.39	1.13	.84	1.69	1.53	54	52.5	50	45.5	39.5
5810	.37	2.01	.82	1.70	1.48	53.5	51.5	47.5	42.5	34.5
5811	.36	2.92	.92	1.70	1.59	53.5	50.5	45	38.5	31
5963 [1]	.69	1.17	1.28	2.31	5.78	60.5	56	51.5	46.5	39.5
5964 [1]	.75	2.68	1.34	2.56	5.93	60	55.5	48.5	43.5	37.5
5965 [1]	.82	4.07	1.35	2.60	5.77	61.5	55.5	48	41.5	35.5

[1] Heated to 2250° F., instead of 2350° F. to avoid melting the steel.

It can readily be seen in each of the above groups, that as the chromium increases from about 1.0 to 4.0% the hardness decreases for a given reheating temperature above about 1200° F.

It, therefore, appears that some other factors evidently control the hardness of the steel after tempering, and I have discovered the principle that the resistance to softening, rather than being

TABLE II

Effect of vanadium on hardness of steels after tempering

Bar	Analysis, Per Cent					Rockwell C Hardness, After Cumulative 2 Hour Temperings At—				
	C	Cr	V	W	Mo	1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
5854	.42	1.28	.99	.96	1.40	54.5	53	50	45.5	38.5
5858	.39	1.23	1.40	.95	1.44	54.5	52.5	48	43.5	38
5856	.41	1.32	.93	1.71	.79	53.5	50.5	49	46	38.5
5860	.39	1.36	1.39	1.71	.78	54.5	52	48	44.5	39.5
5855	.42	1.33	.98	2.83	1.46	56	54.5	51.5	47.5	40
5859	.44	1.37	1.43	2.81	1.45	56	53.5	49.5	45.5	40

Although the effect with vanadium is not so marked as it is with chromium, the tendency is clearly indicated in Table II particularly for reheatings at 1250° and 1300° F., namely, that increasing the vanadium content from about 0.9 to 1.4% causes a decrease in hardness.

It was also found to be true, as shown in Table III, that steels containing large totals of Cr, V, W, and Mo were less resistant to softening, particularly at temperatures over about 1200° F., than steels containing smaller total amounts of these elements.

TABLE III

Effects of combinations of Cr, V, W, *and* Mo *on hardness of steels after tempering*

Bar	Analysis, Per Cent					Sum Of Cr, V, W, Mo	Rockwell C Hardness, After Cumulative 2 hour Temperings At—				
	C	Cr	V	W	Mo		1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
5855	.42	1.33	.98	2.83	1.46	6.60	56	54.5	51.5	47.5	40
5856	.41	1.32	.93	1.71	.79	4.75	53.5	50.5	49	46	38.5
5854	.42	1.28	.99	.96	1.40	4.63	54.5	53	50	45.5	38.5
5680	.40	2.34	.90	3.28	2.85	9.37	56.5	50	45	41.5	37
5862	.39	1.28	1.50	2.79	2.41	7.98	54	49.5	45	40	34
5811	.36	2.92	.92	1.70	1.59	7.13	53.5	50.5	45	38.5	31

It is clear from this table that steels of the first group containing the carbide forming elements between 4.6 and 6.6% in aggregate, have much better resistance to softening above 1200° F. than steels of the second group containing these elements between 7.1 and 9.4% in aggregate.

All of the data given above serve to negate the generally accepted opinion that increasing amounts of carbide forming alloying elements, directly proportional to the total of the carbide forming elements, is dependent on certain ratios of these elements and the carbon content of the steel. As stated by Crafts and Lamont in Tech. Pub. 2439, AIME, 1948, the probable formulae of the carbides of chromium, vanadium, tungsten and molybdenum in the steels which have secondary hardening, are, respectively, Cr_7C_3; V_4C_3; W_2C and Mo_2C. The proportions by weight of carbon in these compounds are .10×percent Cr for the carbide Cr_7C_3; .18×percent V for the carbide V_4C_3; .03×percent W for the carbide W_2C and .06×percent Mo for the carbide Mo_2C. Now, I have discovered that if the composition of the steel is so balanced that the carbon content thereof is approximately equal to the total carbon which can combine with the elements chromium, vanadium, tungsten and molybdenum according to the carbide formulae given above, then the resistance of the steel to softening will be greatly enhanced. On the other hand, if the

composition is such that the carbon content is appreciably less than the total amount that can combine with the elements, Cr, V, W, and Mo, according to the above formulae, then the resistance to softening is relatively poor.

Before presenting test data in support of this statement, consider for a moment how the formula works out for a well known commercial steel, viz., 18–4–1 high speed, as compared to a steel in accordance with the present invention, as set forth in the following Table IV.

TABLE IV

	Analysis, Per Cent					Amounts of C Which Could Combine With Elements As Carbides				Total Amount Of Carbon Which Could Combine With Elements, T	Total Which Could Combine minus Actual Carbon, T–C
	C	Cr	V	W	Mo	Cr_7C_3 .10×Cr	V_4C_3 .18×V	W_2C .03×W	Mo_2C .06×Mo		
18–4–1 High Speed Steel	.72	4.1	1.0	17.6	0.4	.41	.18	.53	.02	1.14	+.41
Steel of Invention	.56	1.3	1.3	2.8	1.5	.13	.23	.08	.09	.53	−.03

In the steels of this table, the balance of which is iron, in each instance, the compositions of the carbide forming elements of the steels are given first; then follows the amounts of carbon which could combine with each of the elements in the steel according to the formulae given above; then, in the second column from the right, the total amount of carbon which could combine with the chromium, vanadium, tungsten and molybdenum in the steel is given under the heading "T"; and finally, in the last column at the right, the difference between this total amount of carbon that could combine with the carbide forming elements in the steel, T, and the actual amount of carbon, C, in the steel is given under the heading "T–C." As shown in Table IV, for the commercial 18–4–1 high speed steel the carbon content is considerably less than the total carbon required completely to combine with the carbide forming elements present. Therefore, the value of T is appreciably higher than the value of C, and the difference between the two, T–C, is plus 0.41. On the other hand in the steel of this invention, the carbide forming elements are so balanced that the value of T approximates the value of C, the difference between them being only minus 0.03.

Many of the high alloy commercial steels contain so much of the carbide forming elements that the steels are hypereutectic, that is, they contain residual carbides right up to the solidus temperature of the steel. Accordingly, when the steels are heated for hardening, even though they are heated at very high temperatures, all of these elements are not dissolved in the austenite. Consequently the martensite which forms from this austenite when the steel is cooled to room temperature, does not contain the maximum of the alloying elements in the steels. Since the resistance to softening depends on the precipitation of alloy carbides in the tempering of the martensite, the full advantage of the alloying elements is not attained unless these elements had previously been dissolved in the austenite. In order to measure the optimum resistance to softening, it is desirable, therefore, to heat the steels just short of the solidus temperature, and then quench and reheat them, and test for hardness after successively higher reheating temperatures.

Such a procedure was carried out for a series of commercial steels and for steels of this invention. In order to make the comparison as fair as possible, all steels with one exception, were heated to 2350° F., which is close to the maximum temperature permissible for 18–4–1 high speed steel. The other steel, a vanadium-molybdenum, high speed steel, was heated to 2225° F., approximately the solidus temperature of this steel. The steels were then quenched and reheated cumulatively for periods of two hours each, at temperatures ranging from 1150° to 1350° F., in fifty-degree intervals, and tested for hardness after each reheating. The results are shown in the following Table V.

TABLE V

Comparison of resistances to softening at temperatures from 1150° to 1350° F. of steels of this invention, and commercial steels

[All steels except as noted were heated to 2350° F.; quenched; and then reheated as indicated.]

	Analysis, Per Cent								Rockwell C Hardness, After Cumulative 2 hr. Temperings at —				
	Bar	C	Cr	V	W	Mo	T	T–C	1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
This invention	5,955	.56	1.26	1.33	2.78	1.52	.54	−.02	59	56.5	52.5	47.5	43.5
Do	2,222	.57	1.35	1.36	1.22	2.38	.57	.00	59	56	52.5	47.5	41.5
Do	2,224	.50	1.35	1.38	2.26	1.93	.58	+.08	57.5	54.5	50	46.5	42
Do	5,854	.42	1.28	.99	.96	1.40	.42	.00	54.5	53	50	45.5	38.5
Do	5,805	.41	1.25	.56	.95	.75	.31	−.10	48.5	47.5	44.5	41	33.5
Do	5,905	.43	2.23	.59	.98	.70	.40	−.03	50	46.5	41.5	37.5	32.5
Commercial Steels													
18–4–1 High Speed	8,826	.72	4.07	1.04	17.58	.41	1.15	+.43	60	52.5	47.5	42.5	38.5
8Mo–2V High Speed	[1] 7,052	.85	4.21	2.06	-------	7.54	1.24	+.39	58.5	50.5	45.5	42	38.5
14W–2Cr Hot Work	5,336	.39	2.10	.24	11.42	-------	.59	+.20	55	48.5	41.5	38.5	34.5
9W–3Cr Hot Work	5,029	.29	3.26	.21	8.88	-------	.64	+.35	48	44	39.5	35	29.5
4W–5Cr Hot Work	5,333	.38	5.29	-------	4.34	-------	.66	+.28	45	42	34.5	31.5	28.5
5Cr–Mo–V Hot Work	5,087	.39	5.13	.36	-------	1.35	.65	+.26	46	40	33.5	31.5	28.5
5Cr–W–Mo Hot Work	5,332	.33	4.90	-------	1.14	1.18	.59	+.26	41.5	37.5	31.5	28.5	26.5

[1] Heated at 2225° F.

It will be noted that the first four steels representative of this invention in this table have

better resistances to softening at temperatures over 1150° F. than 18–4–1 high speed steel. This in itself is remarkable, because 18–4–1 high speed steel has long been considered an outstanding material in this respect. It is even more remarkable when consideration is given to the fact that the alloy contents of the steels of this invention are so much lower than those of the 18–4–1 high speed steel. Furthermore, steels 5805 and 5905 representative of this invention, have, despite their very low alloy contents, better resistances to softening them all the commercial steels except the much more highly alloyed high speed steels, and the 14% W hot work steel. The savings in vanadium and tungsten that are possible in the steels of this invention are of considerable strategic value to the United States of America in times of emergency.

It will be noted in Table V that all of the commercial steels have values of (T–C) which are plus 0.20, or higher; whereas the steels of this invention all have values of (T–C) less than plus 0.10. In all the steels of this invention I keep the (T–C) values under plus 0.15.

contains alloying elements in amounts greater than necessary to combine with the carbon in the ratios mentioned above, that is, when the composition is so balanced that the value of T–C is greater than about plus 0.15%, the growth of the alloy carbide particles seems to be facilitated. On the other hand, if the steel contains just enough or somewhat less than enough of the alloying elements to combine with the carbon, that is, when the composition is so balanced that the value of T–C is zero or less, the growth of the alloy carbide particles is retarded. Furthermore it appears that the more complex the composition, that is, the greater the number of the alloying elements the steel contains the more difficult it is for the carbide particles to grow, and, therefore, the more resistant to softening the steel is.

For this reason I prefer the steels of this invention to contain all of the carbide forming elements referred to previously, namely, chromium, vanadium, tungsten and molybdenum, rather than just one or two of them. The effectiveness of the larger number of these elements is shown in Table VI.

TABLE VI

Effect of four versus three carbide forming elements on the resistance to softening of the hardened steels

Bar	Analysis, Per Cent						T	T–C	Rockwell C Hardness, After Cumulative Tempering					
	C	Cr	V	W	Mo	Bal.			1100° F.	1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
2224	.50	1.4	1.4	2.3	1.9	Fe	.58	+.08	59	57.5	54.5	50	46.5	42
2220	.48	1.4	1.4	------	2.9	Fe	.57	+.09	58	55.5	52.5	47.5	43.5	39

It will be further noted in Table V, that the higher the T value in the steels of this invention the higher the hardness. For applications, where wear resistance is of prime importance I, therefore, balance the steel to have a high T value, and where toughness is the more important requirement, I keep the T value low. Generally for reasons of alloy economy and proper balance of hardness and toughness I prefer the T values to range between 0.3 and 1.00. Since the carbon contents of the steels of my invention are close to the T value, I limit the T value to a maximum of 1.00 for the purpose of maintaining good forgeability of the steels. However I do not confine myself to the use of these steels in the forged condition because I have made useful hot working tools of sand castings of the steels of this invention.

Although it is not yet altogether clear what the mechanism is that controls the resistance to softening of steels of the type being discussed, it seems reasonable to conclude that the "secondary hardening" when the steel is reheated at temperatures above about 900° F. is attributable to the precipitation of alloy carbides, and that the subsequent softening when the steel is heated at higher temperatures is attributable to the agglomeration and growth of these carbide particles. Since it is true that some steels soften much more rapidly with a given heating than others, it seems reasonable to assume that some alloy carbides are more resistant to growth than others, and that this resistance to particle growth, which accounts for resistance to softening, is attributable to the composition of the steel. When the steel

It seems clear from this tabulation that even though the T and T–C values are practically the same for both steels, Bar 2224 containing all four alloying elements is more resistant to softening at temperatures over 1100° F., than Bar 2220 which contains only three of the alloying elements.

Since the carbon factors for the elements vary from 0.3 for tungsten to .18 for vanadium, I consider it desirable to vary the contents of these elements in the steels of this invention so that the carbon combined with each element is at least about .03%. Thus the lower limits for these elements would be about 0.3% for chromium; 0.2% for vanadium; 1.0% for tungsten; and 0.5% for molybdenum. In addition, and in order to insure adequate hardenability of the steel, chromium should be present in amounts greater than about 0.5%.

Since the carbon content of the steel must increase according to the formula with increase of the carbide forming elements, and since the toughness of the steel diminishes with increase of carbon, I maintain the upper limits of the alloy contents so that the carbon combined with each element is generally no greater than about 0.3%. This sets the upper limits of the elements to about 3.0% for chromium; about 2.0% for vanadium; about 10% for tungsten; and about 5% for molybdenum. However, because of the cost and strategic importance of tungsten, I preferably limit the use of the latter element to about 3.0%. Because of the cost factor I also preferably limit molybdenum to about 4%.

Although no mention has been made of manga-

nese and silicon in the steels of this invention it is to be understood that all compositions contain up to about 1.0% of manganese and up to about 2.0% of silicon, the remainder being substantially all iron. The silicon is useful for imparting better scale resistance in some of the compositions used for high temperature bolting service and for hot work forging applications.

I claim:

1. An alloy steel of relatively low alloy content which is hardenable by quenching from an austenitizing temperature, and which undergoes secondary hardening on subsequent tempering at about 1100° F., and which is of a balanced composition such as to impart to said steel in the quenched and tempered condition, high resistance against softening at temperatures upwards of 1100° F., said steel containing about: 0.5 to 3% chromium, 0.2 to 2% vanadium, 1 to 3% tungsten, 0.5 to 4% molybdenum, 0.3 to 1.2% carbon, up to 3% in aggregate of other elements which do not substantially impair said resistance of the steel against softening, and the balance substantially all iron, in proportions such that the sum of $\frac{1}{10}$ of the chromium content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content and $\frac{6}{100}$ of the molybdenum content, shall total at least 0.3% but shall not exceed 0.15% plus the carbon content.

2. An alloy steel of relatively low alloy content which is hardenable by quenching from an austenitizing temperature, and which undergoes secondary hardening on subsequent tempering at about 1100° F., and which is of a balanced composition such as to impart to said steel in the quenched and tempered condition, high resistance against softening at temperatures upwards of 1100° F., said steel containing about: 0.5 to 3% chromium, 0.2 to 2% vanadium, 1 to 3% tungsten, 0.5 to 4% molybdenum, 0.3 to 1.2% carbon, up to 1% manganese, up to 2% silicon, and the balance substantially all iron, in proportions such that the sum of $\frac{1}{10}$ of the chromium content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content and $\frac{6}{100}$ of the molybdenum content, shall total at least 0.3% but shall not exceed 0.15% plus the carbon content.

3. An alloy steel of relatively low alloy content which is hardenable by quenching from an austenitizing temperature, and which undergoes secondary hardening on subsequent tempering at about 1100° F., and which is of a balanced composition such as to impart to said steel in the quenched and tempered condition, high resistance against softening at temperatures upwards of 1100° F., said steel containing about: 1 to 2.5% chromium, 0.5 to 1.5% vanadium, 1 to 3% tungsten, 0.5 to 3% molybdenum, 0.4 to 0.9% carbon, and the balance substantially all iron, in proportions such that the sum of $\frac{1}{10}$ of the chromium content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content and $\frac{6}{100}$ of the molybdenum content, shall total at least 0.3% but shall not exceed 0.15% plus the carbon content.

4. A forgeable alloy steel, of relatively low alloy content, which is hardenable by quenching from an austenitizing temperature, and which undergoes secondary hardening on subsequent tempering at about 1100° F., and which is of a balanced composition such as to impart to the steel in the quenched and tempered condition, high resistance against softening at temperatures upwards of 1100° F., said steel containing about: 0.5 to 3% chromium, 0.2 to 2% vanadium, 1 to 3% tungsten, 0.5 to 4% molybdenum, 0.3 to 1.2% carbon, up to 3% in aggregate of other elements which do not substantially impair said resistance of the steel against softening, and the balance substantially all iron, in proportions such that the sum of $\frac{1}{10}$ of the chromium content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content and $\frac{6}{100}$ of the molybdenum content shall fall within the range of about 0.3 to 1.0%, and shall not exceed 0.15% plus the carbon content.

5. A forgeable alloy steel, of relatively low alloy content, which is hardenable by quenching from an austenitizing temperature, and which undergoes secondary hardening on subsequent tempering at about 1100° F., and which is of a balanced composition such as to impart to the steel in the quenched and tempered condition, high resistance against softening at temperatures upwards of 1100° F., said steel containing about: 0.5 to 3% chromium, 0.2 to 2% vanadium, 1 to 3% tungsten, 0.5 to 4% molybdenum, 0.3 to 1.2% carbon, up to 1% manganese, up to 2% silicon, and the balance substantially all iron, in proportions such that the sum of $\frac{1}{10}$ of the chromium content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content and $\frac{6}{100}$ of the molybdenum content shall fall within the range of about 0.3 to 1.0%, and shall not exceed 0.15% plus the carbon content.

6. A forgeable alloy steel, of relatively low alloy content, which is hardenable by quenching from an austenitizing temperature, and which undergoes secondary hardening on subsequent tempering at about 1100° F., and which is of a balanced composition such as to impart to the steel in the quenched and tempered condition, high resistance against softening at temperatures upwards of 1100° F., said steel containing about: 1 to 2.5% chromium, 0.5 to 1.5% vanadium, 1 to 3% tungsten, 0.5 to 3% molybdenum, 0.4 to 0.9% carbon, and the balance substantially all iron, in proportions such that the sum of $\frac{1}{10}$ of the chromium content, $\frac{18}{100}$ of the vanadium content, $\frac{3}{100}$ of the tungsten content and $\frac{6}{100}$ of the molybdenum content shall fall within the range of about 0.3 to 1.0%, and shall not exceed 0.15% plus the carbon content.

PETER PAYSON.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,565,264 August 21, 1951

PETER PAYSON

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 7, for "it" read *is*; column 7, line 12, for "them" read *than*; column 8, line 49, for "from 0.3" read *from .03*; column 10, line 66, list of references cited for "July 3, 1940" read *July 30, 1940*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of February, A. D. 1952.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.