ported protective effect of injected bone marrow suspensions against acute radiation mortality (*5*). Whether bone marrow suspensions release a humoral agent, as has been postulated in the case of spleen shielding (*6*), or simply provide colonies of undamaged cells for repopulation of irradiated hemapoietic tissues, remains to be established.

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An Investigation of Antimony Oxide as an Opacifier for Porcelain Enamels and Glass[1]

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Experimental work was carried out to determine the feasibility of opacifying porcelain enamels and special glasses by the precipitation of an antimony-bearing phase in the basis composition.

During the period between 1935 and 1940, antimony oxide and sodium antimonate were used extensively in the production of opaque white porcelain enamels. Since 1940, however, zirconium oxide and, even more recently, titanium oxide have practically replaced antimony oxide as the opacifying material in wet-process, sheet-steel enamels, although appreciable quantities of antimony oxide and sodium antimonate still are being used in the dry-process cast-iron enameling industry. The zirconia-bearing and titania-bearing enamels have higher opacity per unit of weight, higher gloss, and, in the case of titania enamels, high resistance to acids. In the case of the conventional antimony-bearing enamels, opacification essentially is accomplished by the physical dispersion of a finely divided antimony compound in the glass. In the case of the titania and zirconia enamels, the mechanism of opacification consists of the precipitation of the opacifying phase during the firing operation. Work was therefore carried out to determine whether glass systems might be developed which would permit the precipitation of an antimony-bearing phase in an enamel-like composition, thereby obtaining higher opacity than is possible with present compositions.

It has generally been agreed (*1, 2*) that, in dealing with recrystallization phenomena, the composition and the time-temperature relationships are important controlling factors in obtaining opacity in, for example, opal glasses. In the production of an opaque glass by recrystallization, another factor—namely, the nature of the crystalline product produced—also is of importance. The size and number of crystallites as well as their composition will influence the opacity of the glass. Blau (*1*) presented an excellent discussion of the effect of inclusions on the opacity of a glass. The opacifying compound in an antimony-bearing enamel has been described variously as antimony pentoxide (*3, 4*) or as an antimony, calcium, oxygen, and fluorine compound of high opacity (*5, 6*). Some confusion also appears to exist as to the exact identity of the compound responsible for the opacity in enamels of the zirconia or titania types (*3, 6, 7*). Opacifying compounds said to be present in the crystalline phase in enamels and opal glasses are sodium fluoride and calcium fluoride.

Kreidl and Weyl (*2*) attributed the importance of the fluoride ion to its small atomic radius and, accordingly, to the strong forces exerted on neighboring atoms. The importance of alumina as a constituent in opal glasses (*2*), in enamels (*7, 8*), and in matte glazes (*9*) has been mentioned. Another oxide generally considered to be important in enamels and opal glasses is zinc oxide. This oxide was stated to increase the rate of crystal growth in opal glasses (*2*), whereas, in zirconia enamels, its effect on opacity apparently was like that of alumina, resulting in a reduction of the solubility of zirconia (*8*). Other materials that have been held to be important in the development of opacity in antimony-bearing enamels include oxidizing agents such as sodium nitrate (*10*), potassium nitrate, or zinc nitrate; calcium compounds such as calcium fluoride (*5, 11, 12*); and sodium silicofluoride (*13*).

This paper covers the experimental results obtained during an investigation of the effect of various additions on the opacity of a high-antimony basis porcelain enamel-like glass. The composition of the glass and the additions were based on a considerable amount of laboratory work of an exploratory nature which led to these trials.

The analyzed composition of the basis enamel used in this investigation was as follows:

Oxide	Amount (%)
Na_2O	20.8
B_2O_3	12.5
SiO_2	46.6
Sb_2O_3	19.1
R_2O_3	0.7
H_2O	0.2

Various oxides or combinations of oxides were added to this composition as opacifiers. In tests in which the addition amounted to 20%, the oxides were added to the raw batch. When the additions amounted to less than 20%, however, they were added to a pre-

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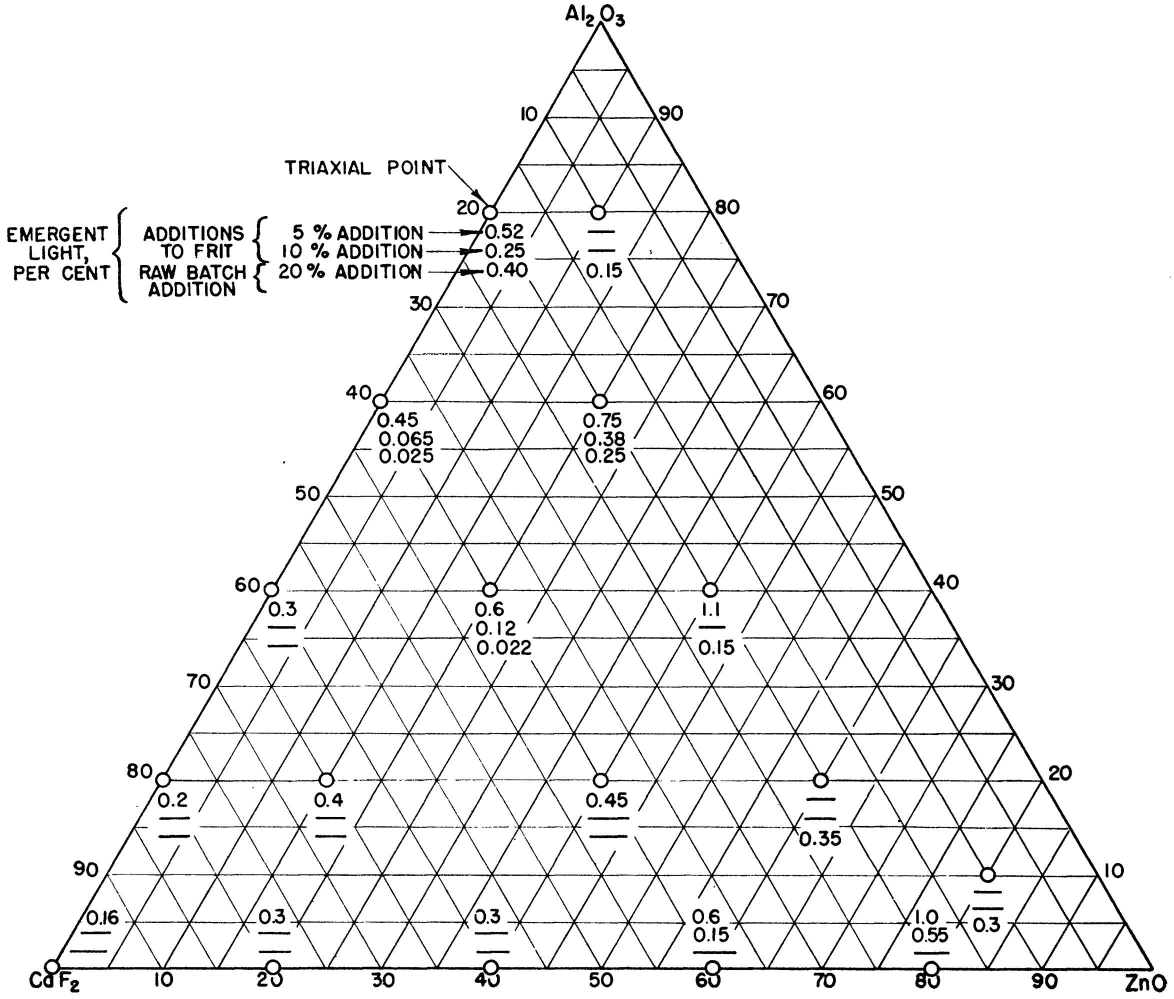


FIG. 1. Translucency of enamel containing antimony oxide plus additions in the system Al_2O_3–CaF_2–ZnO.

viously fritted batch of the basis composition milled to minus 35-mesh size.

The melted or unmelted basis enamel and the desired additives were mixed thoroughly in batches of 150-g size and charged into fire-clay crucibles. The crucibles and their contents were heated in a gas-fired furnace to 1500° F in 2 hr, to 2200° F in another 2 hr, and then held for 1 hr at 2200° F. The resultant melts were pressed into blocks, about 1 1/16" × 7/8" × 1/2", for testing. These blocks were placed in an oven at 500° F, held at this temperature for 1 hr, and then cooled in place to room temperature. Reheating tests were made in an electric furnace for various times and temperatures.

The specimens were evaluated visually, and the opacity was determined by using the translucency meter developed by Haldy, Wright, and Todd (*14*). For the translucency measurements, the specimens were ground, by using a typical horizontal lapping machine, to a thickness of 5 mm, ±0.1 mm, to produce two plane parallel surfaces. The surfaces were finished by using No. 22 Carborundum as the abrasive. Reflectance measurements on these compositions applied as enamels to ground-coated steel were made in the conventional manner of the industry by using a Hunter Multi-Purpose Reflectometer.

Additions of Al_2O_3, CaF_2, and ZnO. Selected mixtures in the system Al_2O_3–CaF_2–ZnO were added in amounts of 5, 10, or 20% to the basis composition containing 19.1% of antimony oxide. The composi-

TABLE 1

COMPOSITIONS USED IN STUDY OF EFFECT OF SMELTING CONDITIONS ON OPACITY

Enamel No.	Composition (% by wt*)					
	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaF_2	**ZnO**
1	45.0	12.0	23.0	12.0	8.0	0.0
2	45.0	12.0	23.0	12.0	4.0	4.0
3	45.0	12.0	23.0	8.0	8.0	4.0
4	45.0	12.0	23.0	8.0	4.0	8.0
5	45.0	12.0	23.0	4.0	4.0	12.0

* Twenty per cent of Sb_2O_3 added to composition based on total batch.

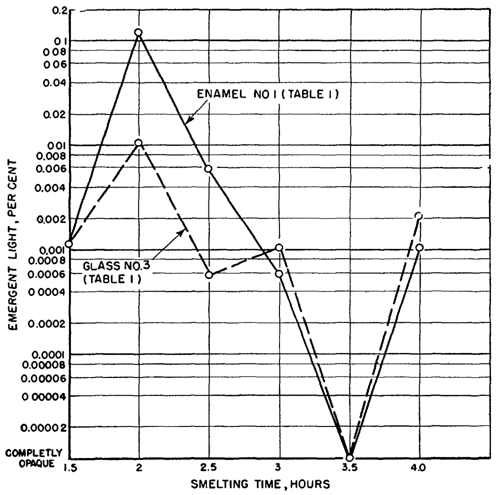
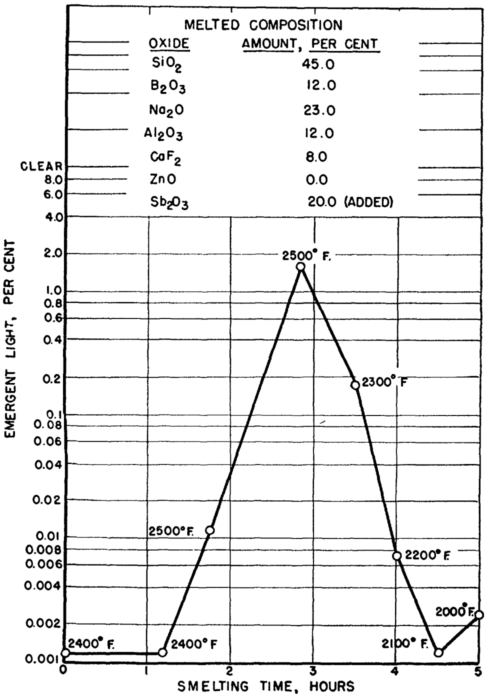


FIG. 2. Effect of smelting time on opacity of an antimony-bearing enamel smelted at 2200° F.

tions of these mixtures and the results of translucency measurements made on the more opaque specimens, after pressing, are shown in Fig. 1. A similar series of tests was made in which these selected mixtures were added to the basis composition containing no antimony oxide.

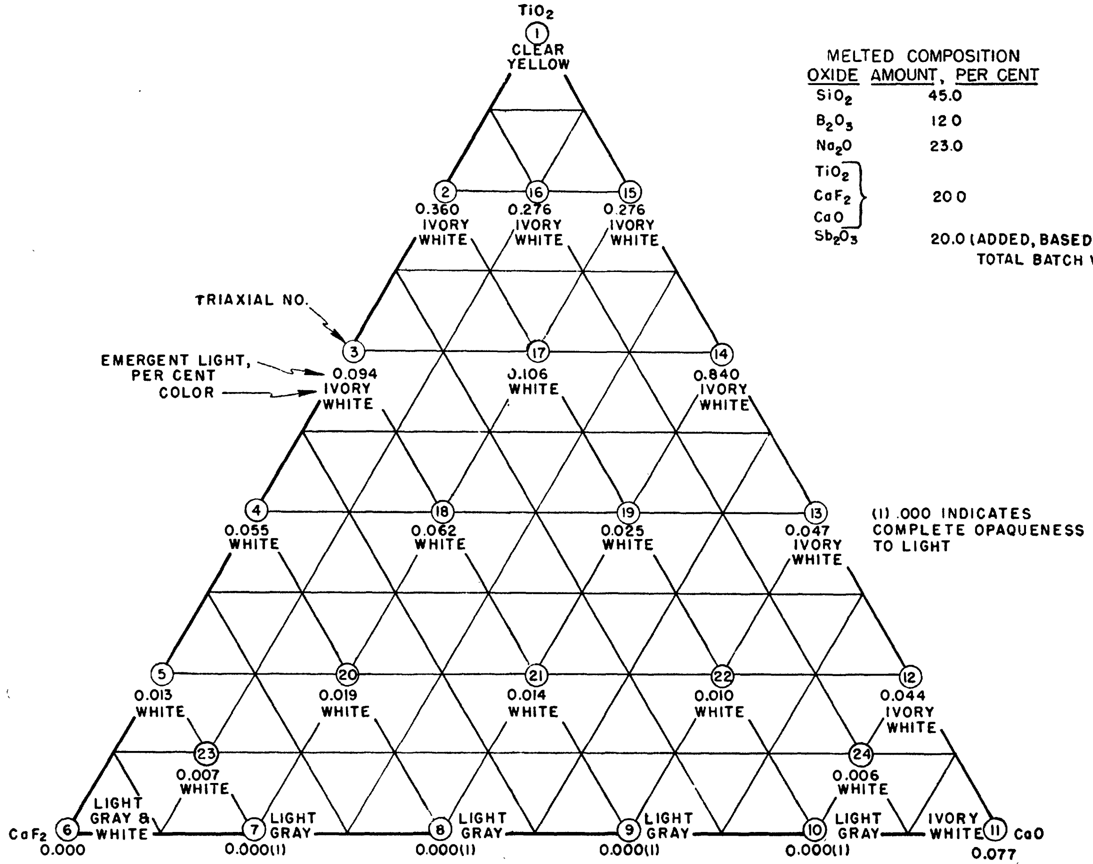
Most of the antimony-bearing melts were opaque.



MELTED COMPOSITION

OXIDE	AMOUNT, PER CENT
SiO_2	45.0
B_2O_3	12.0
Na_2O	23.0
Al_2O_3	12.0
CaF_2	8.0
ZnO	0.0
Sb_2O_3	20.0 (ADDED)

FIG. 3. Effect of variation of smelting temperature and smelting time on opacity.



MELTED COMPOSITION

OXIDE	AMOUNT, PER CENT
SiO_2	45.0
B_2O_3	12.0
Na_2O	23.0
TiO_2 CaF_2 CaO	20.0
Sb_2O_3	20.0 (ADDED, BASED ON TOTAL BATCH WEIGHT)

FIG. 4. Effect of additions of titanium oxide, calcium fluoride, and calcium oxide on opacity.

This opacity was due both to the antimony oxide content and to the addition mixtures; enamels containing no antimony, but containing the various additions, were clear. CaF_2 was the most effective addition in producing opacity; the samples containing no CaF_2 either were clear or were partly translucent. High amounts of CaF_2, in combination with Al_2O_3 and ZnO, resulted in a gray color, which yellowed appreciably on reheating. Whiteness and opacity were obtained, however, if CaF_2 alone, or only small amounts of Al_2O_3 or ZnO, were added with the CaF_2. In these cases, reheating caused no change in the color, but decreased the surface gloss.

The sensitivity of the basis enamel in the development of opacity, when smelted under various conditions, was influenced by the specific additions. Five typical compositions employed in this study are shown in Table 1. The antimony oxide addition was made to the raw batch, and the mixtures were smelted in clay crucibles as before. Two of the compositions exhibited marked variation in opacity when smelted at 2200° F for various times; these results are shown graphically in Fig. 2. When these batches were smelted to the clear state at 2500° F and then cooled to temperatures ranging from 2000° to 2300° F before removal from the furnace, an opacifying phase was precipitated. Data obtained on one of these melts are given in Fig. 3. The other three compositions showed no variation in opacity when smelted at 2200° F for variable times, and no opacifying phase was obtained when these compositions were melted to clear glasses and cooled prior to removal from the furnace.

Additions of Al_2O_3, CaF_2, and CaO. Additions of Al_2O_3, CaF_2, and CaO were made to the antimony-bearing compositions described previously. These additions were the same as shown on the triaxial diagram in Fig. 1, but the ZnO was replaced by CaO.

In general, the antimony-bearing specimens containing Al_2O_3, CaF_2, and CaO were opaque. The color varied from pale-green through grayish-white and ivory-gray to gray. High alumina additions usually resulted in homogeneous mixtures of a pale-green, clear, or translucent glass and a white opaque glass. Large additions of CaF_2 resulted in characteristic gray colors, and CaO produced dense, ivory-white opacity. Melts containing various proportions of CaF_2, CaO, and Al_2O_3 tended to be gray. Reheating caused no apparent change in opacity or color, but resulted in some surface devitrification. Calcium oxide was not as effective as calcium fluoride in producing opacity when added alone.

Additions of Al_2O_3, CaF_2, and TiO_2. Additions of Al_2O_3, CaF_2, and TiO_2 also were made to the antimony-bearing compositions in the same proportions shown in the triaxial diagram of Fig. 1, but with the ZnO replaced by TiO_2. In general, the antimony-bearing enamels containing additions of Al_2O_3, CaF_2, and TiO_2 were opaque and yellowish in color.

Additions of CaO, CaF_2, and TiO_2. Mixtures of CaO, CaF_2, and TiO_2 were added to the antimony-bearing basis enamel in the proportions indicated in the triaxial diagram of Fig. 1, but with Al_2O_3 replaced by TiO_2 and ZnO replaced by CaO. The effects of the additions on translucency and color are shown in Fig. 4.

A relatively large number of white, opaque melts were obtained with specific additions of TiO_2, CaO, and CaF_2. In general, enamels which contained between 4 and 8% of TiO_2, between 4 and 16% of CaF_2, and between 2 and 16% of CaO were the whitest and most opaque. Compositions containing larger amounts of TiO_2 were yellow and not so opaque; those containing larger amounts of CaO were ivory-white in color and were highly opaque; and those containing greater amounts of CaF_2, although extremely opaque, were gray in color.

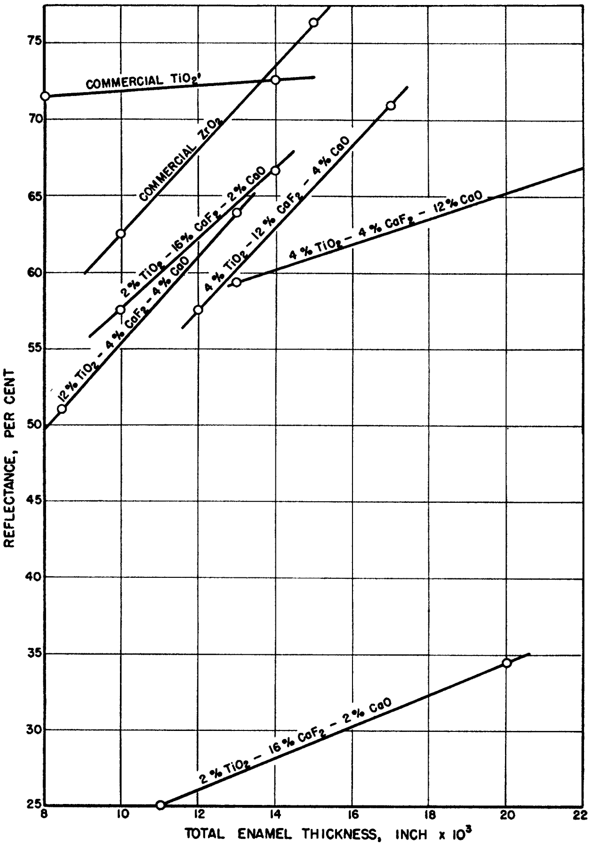


FIG. 5. Reflectance of experimental enamel compositions.

Five of the most opaque of these compositions were smelted on a larger scale for application to steel in the usual commercial manner; in this work, 2400-g batches were employed. Colorless melts were obtained in these tests when a faster melting schedule was used than in the experimental tests, but good opacity was developed when the experimental melting schedule was employed. The melts were fritted, milled, and sprayed on ground-coated steel panels in the customary manner. Magnesium carbonate and clay were employed as the mill additions, but no added opacifier was used. The reflectances of the fired coatings were determined and compared with standard commercial enamels. The results are shown in Fig. 5.

Reflectances between 60 and 70% were obtained with three of the experimental compositions applied to thicknesses of 0.012″–0.014″. Commercial enamels opacified with zirconia or titania, however, were more opaque at lower weights of application.

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Some Patterns of the Respiratory Pigments of Ascites Tumors of Mice

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Inasmuch as we are now able to record accurately the visible and ultraviolet spectra and reactions of the pyridine nucleotides and the cytochromes of various tissue homogenates and intact cells (*1*), it is of interest to compare the pattern of the respiratory pigments of such normal cells with those of neoplastic cells. The ascites tumor, as described recently by Klein (*2*), is the most suitable type of material for our studies since viable and transmissible tumor cell suspensions are obtained in adequate quantities from a single mouse, and the intact cells are studied directly by our methods, without the need for homogenization, as would be necessary with solid tumors. A further advantage of these cells is that they are maximally dedifferentiated.[2]

The mice[3] were sacrificed on the sixth to fifteenth day after inoculation, the tumor cells were freed from erythrocytes by osmotic shock (differential lysis), and the hemoglobin was largely removed by subsequent washing at 0°. The tumor cell counts then averaged about $5 \times 10^4/\text{mm}^3$ for the Ehrlich and Krebs 2 suspensions, and the Q_{O_2} was about 3 at 25° with glucose as a substrate. Successful results were obtained with three tumor cell types: Ehrlich, Krebs 2, and *dba* thymoma ascites (*3*).

The changes in optical density measured here are those that occur upon the exhaustion of the oxygen dissolved in the cell suspension. The normal respiration of our cell suspensions causes anaerobiosis to occur in several minutes. At that time those pigments oxidized by respiratory activity become reduced. A typical experiment is represented by Fig. 1, where the respiration is automatically recorded from polarographic analyses with a platinum electrode. There is no deflection of the spectrophotometric trace in the steady-state oxidized system, but, upon exhaustion of the oxygen, there is a reduction of cytochrome a_3 (a downward deflection of the trace at 445 mμ corresponds to an increase of optical density) and of pyridine nucleotide (an upward deflection of the trace at 340 mμ corresponds to an increase of optical density). The complete spectrum representing the difference between the reduced and the steady-state oxidized condition of the respiratory pigments is obtained by repeating the experiment of Fig. 1 at various wavelengths or by using a continuous recorder (*4, 5*).

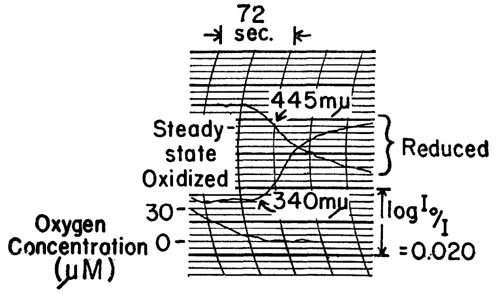

Fig. 1. An illustration of the spectrophotometric measurement of optical density changes in a respiring ascites tumor cell suspension that are coincident with the termination of the oxidase activity. An upward deflection of the traces at 340 mμ represents an increase of optical density, whereas a downward deflection at 445 mμ represents an increase of optical density; *dba* thymoma, cell count, $1.7 \times 10^5/\text{mm}^3$. (Expt 921–12.)

Our results for Krebs 2 ascites tumor cells are given in Fig. 2. These spectra are dominated by cytochrome *c*; the strong visible bands at 549.5, 520, and the Soret

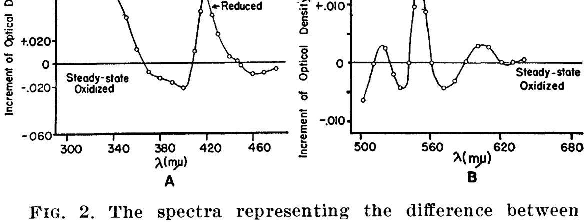

Fig. 2. The spectra representing the difference between the reduced and steady-state oxidized respiratory pigments of Krebs 2 ascites tumor; cell count, $5.8 \times 10^4/\text{mm}^3$. (Expt 921–4.)

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[1] Lalor Foundation predoctoral fellow.

[2] Dale Coman kindly suggested the use of ascites tumor.

[3] T. S. Hauschka, of the Cancer Research Institute, Fox Chase, Pa., very kindly supplied us with mice inoculated with Ehrlich, Krebs 2, and *dba* thymoma ascites.