Comments on the Use of the Lovibond System

Dear Sir: May I be allowed to comment on the article by D. R. Erikson entitled "Finished Product Testing" in the November 1967 issue of the Journal? This contains the remark "The use of Lovibond glasses is limited in that brown or green pigments will interfere with the yellow or the red comparison."

This is quite true when describing the manner in which Lovibond glasses are used in the official Methods of the Society, but is wholly untrue of the Lovibond system as it is intended to be used.

The reason that the AOCS decided—very many years ago—to use the Lovibond scale in a way peculiar to themselves was perfectly valid, and the method as adopted is wholly practical.

Color is three-dimensional, and can only be described or specified in terms of three figures. The Lovibond system is based on three subtractive primaries, (red, yellow and blue as popularly described) and when thus used can accurately measure and define any color.

The scale was designed so that equal values of all three together produced a neutral tint. Hence, if unequal values of all three are used together, the amount of the lowest value represents neutral (dullness) and the balance is the visual color of the sample.

For reasons of ease in handling, the AOCS decided to ignore the brightness factor in this test, and judge only the hue and saturation (chroma). The eye and brain together can do this, whereas it is much more difficult instrumentally. To help in this assessment, separated fields of view were introduced, so as to reduce brightness discrimination.

A further simplification was also introduced. Whereas to match a color *exactly* all the parameters should be variable, it was decided that it was only the redness which was of interest in the special circumstances of the AOCS requirements. Yellow was necessary to make the colors look similar, and thus allow of the redness assessment, but the amount of yellow was unimportant. Therefore the use of a fixed yellow value was adopted, only the red being viewed critically.

For the special requirements of the AOCS test, all this is perfectly valid and works well as a simplified evaluation test.

Unfortunately, many people are prone to make statements, such as was made in Erikson's paper, which emphasize the inadequacies of the AOCS system, and at the same time fail to explain that the inadequacies are not due to the system as originally established by the Tintometer Limited, who have conscientiously pointed out this situation to the Oil Chemists' Society and to the users of this equipment.

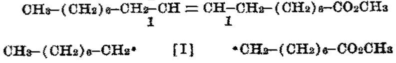
My anxiety is that the statement as published gives the impression that the Lovibond system is incapable of measuring any "off hues" of oils, and in fact in the next sentence the author suggests that because of this defect the Lovibond system should be replaced. It is the special method of using Lovibond glasses (perfectly valid in itself) which gives rise to this defect.

A correctly used Lovibond system can give a complete definition of color and can be converted to C.I.E. coordinates, as can a spectrophotometric result. If you take one of the wheels off a tricycle, it is not then reasonable to complain that you cannot ride it.

G. J. Chamberlin
The Tintometer Limited
The Colour Laboratory
Waterloo Road
Salisbury, England

Thermal Decomposition of Methyl Oleate

Sir: On heating methyl oleate at 280C in an inert atmosphere we could isolate the following compounds as principal decomposition products: methyl decanoate, 9-octadecene, dimethyl 9-octadecene-1,18-dioate, 9,17-hexacosadiene, methyl 9,17-hexacosadienoate and dimethyl 9,17-hexacosadiene-1,26-dioate (Sen Gupta, Fette, Seifen, Anstrichmittel *68*, 475, 1966). A part of the methyl oleate dimerized. The structure of the dimers was dealt with in a later publication (Sen Gupta, Fette, Seifen, Anstrichmittel *69*, 907, 1967). Basing on the structure of the above mentioned main decomposition products and also on some additional experimental evidence we suggested a mechanism of the thermal decomposition of methyl oleate (Sen Gupta, Fette, Seifen, Anstrichmittel *68*, 475, 1966), according to which the C-C bonds alpha to the double bond are homolytically cleaved with production of 4 free radicals [I–IV]. Various reactions of these radicals lead to the compounds isolated.



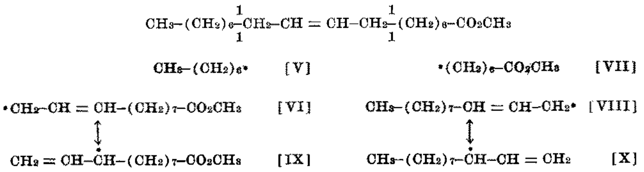
$$CH_3{-}(CH_2)_6{-}CH_2\mid{-}CH = CH{-}\mid CH_2{-}(CH_2)_6{-}CO_2CH_3$$

$$CH_3{-}(CH_2)_6{-}CH_2\cdot \quad [I] \qquad \cdot CH_2{-}(CH_2)_6{-}CO_2CH_3 \quad [III]$$

$$\cdot CH = CH{-}(CH_2)_7{-}CO_2CH_3 \quad [II] \qquad CH_3{-}(CH_2)_7{-}CH = CH\cdot \quad [IV]$$

In a recent publication Nawar and Dubravcic (Nawar and Dubravcic, JAOCS *45*, 100, 1968) suggest—without presentation of new data—an alternative mechanism for the formation of the compounds we isolated from heated methyl oleate. This is based on a splitting of the C-C bonds beta to the double bond. Under these circumstances we feel obliged to communicate that we did consider the suggested alternative mechanism before our paper (Sen Gupta, Fette, Seifen, Anstrichmittel *68*, 475, 1966) was published but decided to reject it on grounds of the following considerations:

1) β-cleavage, as suggested by the authors (Nawar and Dubravcic, JAOCS *45,* 100, 1968), would give rise to two allyl radicals VI and VIII. Since allyl radicals are known to be resonance stabilized (Walling and Huyser in "Organic Reactions," John Wiley & Sons, New York, 1963, Vol. 13, p. 103), it is to be expected that a large part of VI and VIII would exist and react as IX and X. Reaction products of IX and X would invariably be branched chain compounds which we could not detect in the reaction mixture.



$$CH_3-(CH_2)_6\overset{1}{\underset{1}{-}}CH_2-CH=CH-CH_2\overset{1}{\underset{1}{-}}(CH_2)_6-CO_2CH_3$$

$$CH_3-(CH_2)_6\cdot \quad [V] \qquad \cdot(CH_2)_6-CO_2CH_3 \quad [VII]$$

$$\begin{array}{lclc}
\cdot CH_2-CH=CH-(CH_2)_7-CO_2CH_3 & [VI] & CH_3-(CH_2)_7-CH=CH-CH_2\cdot & [VIII] \\
\updownarrow & & \updownarrow & \\
CH_2=CH-\dot{C}H-(CH_2)_7-CO_2CH_3 & [IX] & CH_3-(CH_2)_7-\dot{C}H-CH=CH_2 & [X]
\end{array}$$

2) Resonance stabilized allyl radicals are furthermore known (Walling, "Free Radicals in Solution," John Wiley & Sons, New York, 1963, p. 47) to dimerize easily. Dimerization of VI, VIII-X would lead to C_{22} hydrocarbons and C_{22} dibasic acids neither of which could be detected among the decomposition products of methyl oleate.

3) The formation of methyl decanoate can hardly be explained by the assumption that radicals V and VII each lose a moiety of ethylene to give pentyl and ω-carbomethoxy butyl radicals which then combine (Nawar and Dubravcic, JAOCS *45,* 100, 1968). Intercombination of V, VII, pentyl and ω-carbomethoxy butyl radicals must then logically be expected to give appreciable amounts of tetradecane, dodecane, decane, and the dimethylesters of C_{10}, C_{12}, C_{14} dibasic acids. This, however, was not observed.

4) The formation of the C_{26}-compounds is a remarkable phenomenon in the thermal decomposition of methyl oleate. Our experimental evidence, particularly the formation of methyl 15-tetracosenoate on heating methyl palmitate with methyl oleate (Sen Gupta, Fette, Seifen, Anstrichmittel *68,* 475, 1966) proves that the terminal ethyl group of esters or of hydrocarbons is converted to an unsaturated center which then adds octyl or carbomethoxy heptyl radicals to give the long chain compounds. This fact has been overlooked by the authors (Nawar and Dubravcic, JAOCS *45,* 100, 1968) altogether. The formation of methyl 15-tetracosenoate cannot be explained by the suggested alternative mechanism.

5) Our work has shown that there is a great difference of reactivity between the vinyl radicals II and IV. II is a vinyl radical with an ester group in the molecule and this is converted by hydrogen abstraction to the saturated methyl decanoate in good yield while IV does not produce any appreciable amounts of decane. This is a fact of primary importance which should not be neglected. The presence of the ester group in methyl oleate may possibly diminish the energy required for a vinyl splitting of the aliphatic chain. As far as we know, no data on the energy of homolytic chain cleavage of fatty esters are available. These may be substantially lower than those determined for hydrocarbons. The validity of this argument is demonstrated by the fact that unsaturated hydrocarbons do not show any chain cleavage at 220C (Sen Gupta, unpublished results on heating of 9-octadecene) at which temperature methyl oleate decomposes under chain cleavage (Sen Gupta, Fette, Seifen, Anstrichmittel *69,* 907, 1967).

A. K. Sen Gupta
Unilever Forschungslaboratorium
Behringstrasse 154
2 Hamburg 50, Germany

Coconut Oil and Filled Milk

Sir: The article on coconut oil which appears on page 218A of the April, 1968, issue of *JAOCS* has been called to my attention.

The article states that coconut oil is assuming new status because of a new dairy product called "filled milk." The use of coconut oil, according to the article, provides "a milk product which has better keeping qualities, costs less and is lower in saturated fats which are usually connected with arteriosclerosis."

Aside from the fact that there is still a great deal of controversy about whether fats in the diet are related to heart disease, it is also a fact that coconut oil is more highly saturated than butter fat. Further, coconut oil is more hypercholesteremic (causes a greater rise in blood cholesterol levels) than butterfat. Therefore, coconut oil could hardly be desirable for persons trying to reduce their intake of saturated fats or lower their blood cholesterol levels.

Louis B. Raffel
National Dairy Council
Chicago, Illinois